ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

* The year is not inserted in references to 1920

ABBREVIATED TITLE.	JOURNAL
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
D.R.-P.	Deutsches Reichs-Patent.
Deutsch. med Woch.	Deutsche medizinische Wochenschrift.
Fuhlings Landw. Zeit.	Fuhlings Landwirtschaftliche Zeitung.
Gazzetta	Gazzetta chimica italiana
Gesundheits-Ing.	Gesundheits-Ingenieur.
Helv. Chim. Acta	Helvetica Chimica Acta
Int. Mitt. Bodenk.	Internationale Mitteilungen fur Bodenkunde.
Int. Zeitsch. phys. - chem. Biol.	Internationale Zeitschrift fur physikalisch-chemische Biologie.
Jahrb. Min.	Neues Jahrbuch fur Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil. Bd.	Neues Jahrbuch fur Mineralogie, Geologie und Palaeontologie; Beilage Band.
Jahrb. Radioaktiv. Elek-tronik	Jahrbuch der Radioaktivitat und Elektronik.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society
J. Amer. Pharm. Soc.	Journal of the American Pharmaceutical Association
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Biol. Chem	Journal of Biological Chemistry.
J. Chim. phys.	Journal de Chimie physique
J. Gasbeleucht.	Journal fur Gasbeleuchtung und Wasserversorgung.
J. Gen. Physiol.	Journal of General Physiology
J. Ind. Eng Chem.	Journal of Industrial and Engineering Chemistry.
J. Ind. Inst. Sci.	Journal of the Indian Institute of Science.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm Expt. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan.	Journal of the Pharmaceutical Society of Japan.
J. Phys. Radium	Journal de Physique et le Radium.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gen.	Journal de Physiologie et de Pathologie générale.
J. pr. Chem.	Journal fur praktische Chemie.
J. Proc. Asiatic Soc. Bengal	Journal and Proceedings of the Asiatic Society of Bengal.
J. S. African Assoc. Anal. Chem.	Journal of the South African Association of Analytical Chemists.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Tokyo Chem. Soc.	Journal of the Tokyo Chemical Society.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Koll. Chem. Beihefte.	Kolloidchemische Beihefte.
Kolloid Zeitsch.	Kolloid Zeitschrift.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Mededeelingen Geneesk. Lab. Weltevreden	Veeartsenijkundige Mededeelingen uit het Geneeskundig Laboratorium te Weltevreden, Batavia.
Mem. Coll. Sci. Kyōtō	Memoirs of the College of Science, Kyōtō Imperial University
Mem. Dept. Agric. India	Memoirs of the Department of Agriculture in India.

ABBREVIATED TITLE.	JOURNAL.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Min Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Mitt. Naturforsch. Ges Halle	Mitteilungen der Naturforschenden Gesellschaft zu Halle.
Monatsh.	Monatshefte fur Chemie und verwandte Theile anderer Wissenschaften
Nachr Ges. Wiss. Göttingen.	Nachrichten von der Gesellschaft der Wissenschaften zu Gottingen
Öfvers. Finska Vet -Soc.	Öfversigt af Finska Vetenskaps-Societetens Forhand-lingar, Helsingfors.
Oesterr. Chem -Zeit	Oesterreichische Chemiker-Zeitung.
P.	Proceedings of the Chemical Society.
Pfluger's Archiv	Archiv fur die gesammte Physiologie des Menschen und der Thiere.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review
Physikal. Zeitsch.	Physikalische Zeitschrift
Proc. Amer Inst. Electrical Engineers	Proceedings of the American Institute of Electrical Engineers
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. Colorado Sci. Soc.	Proceedings of the Colorado Scientific Society.
Proc. Iowa Acad. Sci.	Proceedings of the Iowa Academy of Science.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amster-dam. Proceedings (English version).
Proc Nat. Acad Sci.	Proceedings of the National Academy of Sciences.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Soc Exp Biol. Med	Proceedings of the Society for Experimental Biology and Medicine.
Rec. trav. chim	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Schweiz. Apoth. Zeit.	Schweizerische Apotheker Zeitung.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Tōhoku Imp. Univ.	Science Reports, Tōhoku Imperial University.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Arch. Physiol.	Skandinavisches Archiv fur Physiologie.
Soil Sci.	Soil Science.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
T.	Transactions of the Chemical Society.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Soc. Glass Tech-nology	Transactions of the Society of Glass Technology.
U.S. Pat.	United States Patent
Wien Anz.	Anzeiger der Akademie der Wissenschaften Mathe-matisch-Naturwissenschaftliche Klasse, Wien.
Zeitsch. anal. Chem.	Zeitschrift fur analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift fur angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift fur anorganische und allgemeine Chemie.
Zeitsch. Elektrochem.	Zeitschrift fur Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift fur Krystallographie und Mineralogie.

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GENERAL AND PHYSICAL CHEMISTRY.

THE past year marks the attainment of the pre-war level so far as physical chemistry is concerned. In the new conditions which now obtain, however, this will certainly not represent the average output; a considerable increase may be anticipated in subsequent years, and compilations such as the present will almost certainly have to be expanded to keep pace with the advance.

A great deal of research has been carried out in the field of atomistics, and this is reflected in the present Report, unfortunately to the exclusion of much which should have found a place. It was felt, however, that just now a very limited number of those topics should be dealt with, which, to be understood, could not be treated except in some detail, so as to enable a return to be made eventually to a treatment presenting greater variety and probably, therefore, greater general interest.

Energetics of the Crystal Lattice.

The interest aroused in the problem of the structure of crystals by the pioneer work of Laue and the Braggs has led to an intensive study, in the first instance by Born and later by others, of the mechanics of the lattice, the energy involved in its dissociation into ions, its formation from the elements, and allied problems. The X-ray method has shown that, in general, the atom and not the molecule is the significant material unit. By a refinement of the X-ray method, P. Debye and P. Scherrer [1] have succeeded in showing that the electrons belonging to an atom are concentrated inside a very small space around the nucleus, the radius of the space being

[1] *Physikal. Zeitsch.*, 1918, **19**, 474; *A.*, 1919, ii, 20.

about one-tenth of δ, where δ is the so-called "lattice constant," and denotes the distance between two similar atoms. M. Born[2] has shown further that the atoms in salt crystals are electrically charged; they are, in fact, ions, carrying a charge identical with the charge of an electron in the case of salts of the type of potassium chloride. The properties of the crystal lattice involve a knowledge of the laws of electrical attraction and repulsion existing between any pair of oppositely-charged ions. It has been shown by Born that the attraction follows the ordinary inverse square law, whilst the repulsion varies as the inverse tenth power, or the potential of the repulsive force varies as the inverse ninth power of the distance. On this basis the compressibility of crystals of the cubic type can be accurately computed, as can also the lattice constant.[3]

The fact that the potential of the repulsive force involves an exponent $n = 9$ is of importance in connexion with the structure of atoms in general. Thus Born and Landé[4] have shown that the atomic model of Bohr (in which the electrons revolve in concentric orbits round the nucleus), when applied to crystals, gives rise to $n = 5$, which in turn leads to values for the compressibility which are approximately twice as great as those observed. The discrepancy is so great that in Born's opinion[5] it is necessary to discard the Bohr atomic model. He finds that the cubical atom model of G. N. Lewis leads to the required inverse ninth power relation in the case of crystals. This makes it almost certain that the cubic atom model with electrons moving in restricted or localised paths is in better accord with the facts than is Bohr's model, especially for those cases in which more than one electron is present in the atom. This conclusion will be referred to again in a subsequent section.

On the basis of the above laws of attraction and repulsion, Born[6] has developed the following expression for U, the energy required (strictly at absolute zero) to dissociate completely one gram-molecule of crystal lattice into free ions:

$$U = \frac{Na}{4\delta} \frac{n-1}{n}$$

where N is the Avogadro constant, δ the lattice constant, n the exponent of the potential of the repulsive force, and a is a constant characteristic of the attractive force (attractive force =

[2] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 604; *A.*, ii, 401.

[3] M. Born and A. Landé, *Ber. Deut. physikal. Ges.*, 1918, **20**, 210; *A.*, 1919, ii, 188; M. Born. *Ann. Physik*, 1920, [iv], **61**, 87; *A.*, ii, 227.

[4] *Sitzungsber Preuss. Akad. Wiss. Berlin*, 1918, 1048; *A.*, ii, 424; *Ber. Deut. physikal. Ges.*, 1918, **20**, 202; *A.*, 1919, ii, 188.

[5] *Ber. Deut. physikal. Ges.*, 1918, **20**, 230; *A.*, 1919, ii, 188.

[6] *Ibid.*, 1919, **21**, 13; *A.*, 1919, ii, 214.

a/δ^2). On the basis of this equation Born has calculated the value of U for a considerable number of salts. A few typical results are quoted to give an idea of the order of magnitude involved. The unit of energy is the kilo.-calorie.

Salt.	LiCl.	NaCl.	KCl.	RbCl.	CsCl.	KBr.	KI.
U	179	182	163	155	156	155	144

The accuracy of these values has been tested in an approximate manner by Born by considering a reaction of the type: [NaCl]+ [KI] =[KCl]+[NaI] (the square brackets denote the solid state), in which the net change in U can be equated to the net heat effect, the latter term being obtained by algebraic summation of the individual heats of formation of the salts from their elements. Unfortunately, the net heat effect and net change in U are very small quantities. So far as the comparison goes it is favourable to the lattice theory. Born has attempted to carry out an alternative test by taking into consideration the energy required to ionise the gaseous atoms of the elements from which the salt would ordinarily be formed—it is important to observe that U refers to formation of salt from the free ions and not from the atoms. The results obtained by this method also lend support to the lattice theory. A more exact test of the validity of the equation already given for U has been carried out,[7] based on the heat of solution of salts in water to form very dilute solutions. The results substantiate the theory in a satisfactory manner.

Fajans[8] has further investigated the heat of solution, L, of individual salts, pointing out that this quantity is composed of two effects, (a) the energy required to dissociate the salt into free gaseous ions, namely, U, and (b) the heat evolved when these ions are dissolved in water. The latter effect is regarded by Fajans as "heat of hydration of gaseous ions," the term hydration being taken to mean the condensation of an indefinite (non-stoicheiometric) number of water molecules around the ion as a result of electrostriction. Taking the case of potassium chloride we can write:

$$K^+{}_{gas} \quad + \quad Cl^-{}_{gas} \quad = \quad [KCl]_{solid} \quad + \quad U,$$
$$[KCl]_{solid} \quad + \quad aq. \quad = \quad K^+aq. + Cl^-aq. + L,$$
whence $\quad K^+{}_{gas} \quad + \quad Cl^{-\,+aq}_{\ \ gas} \quad = \quad K^+aq. + Cl^-aq. + U + L.$

From this it follows that $W_{(cation)+(anion)}$, the heat of hydration of both ions, is given by:

$$W_{(cation)+(anion)} \quad = \quad U \quad + \quad L.$$

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[7] K. Fajans, *Ber. Deut. physikal. Ges.*, 1919, **21**, 542 ; *A.*, ii, 21.
[8] *Ibid.*, 549 ; *A.*, ii, 12.

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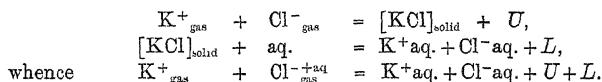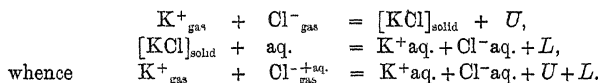[5] *Ber. Deut. physikal. Ges.*, 1918, **20**, 230 ; *A.*, 1919, ii, 188.

[6] *Ibid.*, 1919, **21**, 13 ; *A.*, 1919, ii, 214.

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$$K^+{}_{gas} + Cl^-{}_{gas} = [KCl]_{solid} + U,$$
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whence $\quad K^+{}_{gas} + Cl^{-+aq.}{}_{gas} = K^+aq. + Cl^-aq. + U + L.$

From this it follows that $W_{(cation)+(anion)}$, the heat of hydration of both ions, is given by:

$$W_{(cation)+(anion)} = U + L.$$

[7] K. Fajans, *Ber. Deut. physikal. Ges.*, 1919, **21**, 542; *A.*, ii, 21.
[8] *Ibid.*, 549; *A.*, ii, 12.

The following typical results indicate the extremely high values obtained in this way. The heat of hydration is expressed in kilo.-cal. per gram-molecule.

Salt	LiCl.	NaCl.	KCl.	KBr.	KI.
$W_{(cation+anion)}$	187	180·5	159	150	139

The calculation just given affords values for the heat of hydration of both ions. The heat of hydration of individual ions has been calculated [9] by a method based on measurements of the refractive indices of aqueous solutions of alkali chlorides. The value obtained for the heat of hydration of the chlorine ion itself is 172 kilo.-cal. This is nearly the same as the values quoted above. That is, the cations have a negligible heat of hydration. This is a distinctly surprising result, and must be received with caution.
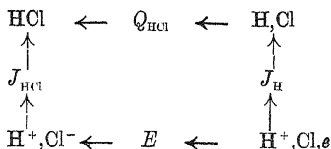
The next problem to which Born,[10] and later Fajans,[11] applied the lattice theory was the calculation of the affinity of neutral halogen atoms for electrons. This affinity is measured by E, where E is defined as the work which must be expended in removing an electron from a halogen ion. Born shows that E is a positive quantity, that is, the neutral halogen atom has a positive affinity for an electron. Born's argument is as follows. We begin with solid potassium chloride and imagine it decomposed into free gaseous ions in two different ways. The first way corresponds with the direct dissociation which involves an absorption of U energy units, 163 kilo.-cal. per gram-molecule. The second way corresponds with the decomposition of the salt into its electrically neutral elements, metallic potassium and gaseous molecular chlorine, whereby Q units are absorbed, namely, 106 kilo.-cal. The potassium is then vaporised, the heat absorbed being about 21 kilo.-cal., and the atoms are ionised into ions and free electrons. The latter process corresponds with the ionisation potential of the metallic vapour, namely, 99 kilo.-cal. At the same time, the molecular chlorine is dissociated into its atoms, the heat absorbed being 53 kilo.-cal. per gram-atom, and each of these atoms attaches to itself one of the electrons set free by the ionisation of the potassium vapour. We have thus arrived at the same end-point by two different paths. Equating the energy terms, it is found that the union of an electron with the chlorine, bromine, and iodine atom, respectively, involves the evolution of 116, 87, and 81 kilo.-cal. per gram-atom. No direct measurement of E is available. Born has tested the accuracy of the calculated value by an indirect method, based on

[9] F. Haber, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 990; *A.*, ii, 244.
[10] *Ber. Deut. physikal. Ges.*, 1919, 21, 679; *A.*, ii, 156.
[11] *Ibid.*, 714; *A.*, ii, 156.

the ionisation of the hydrogen haloids. The mode of ionisation in this case was assumed by Born to be: $HCl \longrightarrow H^{\cdot} + Cl'$, and this assumption was later confirmed experimentally.[12] The corre-sponding energy term we shall denote by J_{HCl}. The various inter-relationships in the case of gaseous hydrogen chloride are con-veniently shown by the following scheme, which is due to Haber[13]:

$$
\begin{array}{ccccc}
HCl & \longleftarrow & Q_{HCl} & \longleftarrow & H,Cl \\
\uparrow & & & & \uparrow \\
J_{HCl} & & & & J_{H} \\
\uparrow & & & & \uparrow \\
H^{+},Cl^{-} & \longleftarrow & E & \longleftarrow & H^{+},Cl,e
\end{array}
$$

Symbols separated by commas indicate free atoms or ions separated by an infinite distance from one another. The direction of the arrows corresponds with an evolution of heat. Incidentally, the quantity J_{HCl} differs from U_{HCl} by an amount identical with the heat of sublimation of hydrogen chloride. Q_{HCl} denotes the heat which would be evolved by the union of atomic hydrogen and atomic chlorine, a quantity which is known to be 117 kilo.-cal. per gram-molecule of hydrogen chloride formed. J_{H} denotes the energy of ionisation of a free hydrogen atom, namely, 310 kilo.-cal. per gram-atom, or 13·4 volts. The symbol e stands for an electron. Passing from the right-hand lower corner of the scheme to the upper left hand by the two paths, and equating the energy terms, it is found that $J_{HCl} = 311$ kilo.-cals., this quantity being based in part on the value of E for chlorine calculated by the lattice theory. 311 Kilo.-cal. corresponds with an ionisation potential of 13·5 volts. Foote and Mohler[12] have found by direct experiment 14 volts. The agreement is satisfactory. It may be mentioned that Cuthbertson's value for the dispersional frequency of hydrogen chloride corresponds with $\lambda = 918·67$ Å. Converting this into frequency, and applying the quantum formulation, we find $Nh\nu = 309$ kilo.-cal., a value which is in very good agreement with that obtained by Foote and Mohler. It is noteworthy that the energy of ionisation of hydrogen chloride into two ions is prac-tically the same as that required for the ionisation of the hydrogen atom into the hydrogen nucleus and a free electron. This means that the affinity of the hydrogen nucleus for an electron is practically the same as the affinity of the hydrogen nucleus for a halogen ion. This is considered in some detail by Haber,[13] who concludes that the heat of formation of all the alkali

[12] P. D. Foote and F. L. Mohler, *J. Amer. Chem. Soc.*, 1920, **42**, 1832 ; *A.*, ii, 660.

[13] *Ber. Deut. physikal. Ges.*, 1919, **21**, 754 ; *A.*, ii, 156.

chlorides in the gaseous state from the gaseous atomic elements is the same as that for hydrogen chloride, namely, 117 kilo.-cal. per gram-molecule of salt. In the course of Haber's considerations, he estimates that the heat of sublimation of the alkali haloids is of the order 60 kilo.-cal., a very large quantity when compared with the corresponding term for the solid hydrogen haloids, namely, 4 to 5 kilo.-cal. Haber shows that the above value for the heat of sublimation of the salts is in agreement with their high sublimation temperature. Further, the heat of sublimation of the alkali chlorides has been calculated to be about 50 kilo.-cal.[14] Haber has succeeded in verifying his value for the heat of sublimation by an alternative mode of calculation, making use of a scheme analogous to that already employed in connexion with gaseous hydrogen chloride.

In the foregoing considerations, the hydrogen chloride appears as a gas, and the energy term J_{HCl} refers to this state. Reis[15] has put forward certain important considerations in connexion with the lattice of the crystalline hydrogen haloids. He points out the low heat of sublimation as compared with that of the alkali haloids, and also the extremely high energy of ionisation (300—320 kilo.-cal.), which is about twice as great as that of the alkali haloids (150—180 kilo.-cal.). He also points out the relatively large molecular volume of the solid hydrogen haloids, and finally concludes that the lattice in these cases must be very different from the lattice in the case of the salts. This difference he attributes, very reasonably, to the existence of molecules, as distinct from ions, as the significant material units composing the lattice in the case of the solid hydrogen haloids. He confirms this view by a consideration of the electric moment of the hydrogen chloride molecule.

Returning to the alkali haloid (ionic) lattice it may be pointed out that Haber has applied the quantum theory to this case in the following ingenious manner. Haber regards the known dispersional frequency v_0 of the solid salt, obtained from measurements of the refractive index, as representing the most violent electronic movement of which the lattice is capable, and therefore corresponding probably with the energy U required for its ionisation. We can thus write $U = Nhv_0$, where $N_\bullet$ is the Avogadro constant and h is Planck's constant. In the case of potassium chloride (sylvine), the limiting wave-length λ_0, which corresponds with v_0, has been found to be $160.7 \mu\mu$, λ_0 for rock-salt being

[14] A. Reis, *Zeitsch. Physik*, 1920, **1**, 204 ; *A.*, ii, 537.

[15] *Zeitsch. Elektrochem.*, 1920, **26**, 408 ; *Zeitsch. Physik*, 1920, **1**, 299 ; *A.*, ii, 751.

$156 \cdot 3 \ \mu\mu$. Hence $Nh\nu_0$ for potassium chloride and for sodium chloride is calculated to be 177 and 182 kilo.-cal. respectively, whilst U, as calculated by Born, is 163 and 182 kilo.-cal. respectively. The agreement is striking. In the case of other salts for which Born has calculated U, the necessary refractive index measurements have not been made. Haber, however, makes use of his "square root rule," which connects the known characteristic infra-red vibration frequency of a salt, as determined by Rubens, with the quantity ν_0, and thus calculates approximate values for $Nh\nu_0$, which are compared with U in the following table:

Salt	NaCl.	KCl.	KBr.	KI.	TlCl.	TlBr.	TlI.	LiF.
$Nh\nu_0$ kilo.-cal.	173	165	151	141	144	157	142	336
U_{Born}, kilo.-cal.	182	163	155	144	169	163	151	231

With the exception of lithium fluoride, where the discrepancy is enormous, the agreement is fairly satisfactory. The calculation serves to link up the frequency of the dispersional electron with the properties of the crystal lattice.

We now pass from a consideration of salts to a consideration of metals. Metals are characterised by their thermal and electrical conducting capacity, properties which were formerly explained on the basis of freely moving electrons, each of which possessed considerable thermal capacity. The determinations of the specific heats of metals, carried out in great detail to test the applicability of the quantum theory, have shown, however, that the heat capacity of electrons is negligible until extremely high temperatures are reached. The free electron theory therefore breaks down. In its place, F. A. Lindemann [16] suggested, several years ago, that a metal consists of two interleaved space lattices, one consisting of metallic ions, the other of electrons. On this basis, the electrical conductivity is due to the movement of the electron lattice as a whole through the ionic lattice. The resistance which the electron lattice experiences is due to vibrations of the ions, which impede the movement of the electron lattice as a result of electrical repulsions. At very low temperatures, however, the vibrations of the ions are small, and the electrical conductivity should be abnormally great. This corresponds with the known supra-conductive state discovered by Onnes at the temperature range $3°$ to $0°$ absolute. If the metal is not pure, the ionic lattice is heterogeneous, and the electron lattice has greater difficulty in moving through it. That is, the presence of an impurity should increase the resistance of a metal, a conclusion which is borne out by

[16] *Phil. Mag.*, 1915, [vi], **29**, 127 ; *A.*, 1915, ii, 47.

experiment.   As the electron lattice moves through the ionic lattice at temperatures above zero, it will transfer to the latter a certain amount of the kinetic energy it has gained from the impressed electric field; in other words, the temperature of the metal will rise as a consequence of the passage of current.   Linde-mann shows, further, that the lattice theory of the metallic state is in agreement with Ohm's law.   As regards thermal conductivity, on the lattice theory heat is transmitted by elastic waves.   The thermal conductivity of a metal may be regarded as the sum of the conductivities of the two lattices.   The thermal conductivity of the ionic lattice is necessarily of the same order as that of a salt crystal, and is therefore negligible at ordinary temperatures. The conductivity of the electron lattice, on the other hand, will be large, for, as Lindemann shows, it will behave like an ionic lattice when the latter is at very low temperature, when such lattices are known to possess high thermal conductivity.   Further, the specific heat of the electron lattice, owing to its high limiting frequency, is extremely small.   Thus, without attributing any measurable heat capacity to the electrons, it is possible to have large thermal conductivity as a whole in the case of a metal.   This is in excellent agreement with the results obtained from measure-ments of specific heats, and constitutes the main advantage of the electron lattice theory, as distinct from the older free electron theory.   Lindemann shows, further, that the lattice theory is capable of explaining the mechanism of the photo-electric effect, even accounting for the difficulty that the energy of the photo-electron is often greater than the incident energy of the light falling on one electron.   On the lattice theory, a large part of the wave-front can act on the electron lattice, setting up an elastic wave sufficiently intense to eject an electron from the lattice.

A lattice theory of metals has also been worked out in some detail by Haber,[17] based directly on Born's concepts.   The lattice in this case consists, of course, of ions and electrons.   Using Born's theory, an expression for U, the lattice energy, can be calculated in terms of the compressibility and atomic volume of the metal. Haber also points out that U can be equated to $D + J_m$, where D is the known heat of sublimation of the metal and J_m the energy of ionisation of the vapour, corresponding with the well-known ionisation potential of the latter.   The agreement between the two modes of calculating U is apparently satisfactory.   The follow-ing typical values, expressed in kilo.-cal. per gram-atom, indicate

that the lattice energy of a metal is of quite the same order of magnitude as that of the haloid salts:

Metal	Li.	Na.	K.	Rb.	Cs.	Ag.	Tl.
U	155	140	123	117	109	243	206

From the values of U it should be possible to calculate, on the basis of Born's lattice theory, the value of the exponent n in the potential of the repulsive force. We have already seen that in the case of most salts $n=9$. Haber finds in the case of the alkali metals that n lies between 2 and 4.

This raises a considerable difficulty, for, as Born has shown, such a value for n would mean that the electrons, instead of being fixed, would be free. To overcome this difficulty, Haber, making use of certain results obtained by Debye, substitutes a movable lattice in place of a statical one, and on this basis works out a number of relations. The problem does not seem, however, to be by any means satisfactorily solved, and as much of it is still speculative, we need not enter into it further here. What seems certain is that a lattice of some kind forms the basis of the metallic state.

The Crystal Lattice and Molecular Magnetic Fields.

In the foregoing section an account has been given of the crystal lattice, the material units of which are ionic, from the point of view of electrostatics. In the present section we review briefly the treatment of the crystal lattice, the material units of which are molecules from the point of view of magnetic forces.

That two electrons rotating in a certain manner with respect to one another will attract or repel with a force varying more rapidly than the inverse square of the distance has long been known. Since the introduction of the idea of moving electrons into atomic and molecular theory, the possibility of such electromagnetic attraction and repulsion playing an important part in chemical change has been recognised. This has been specially emphasised by E. C. C. Baly,[18] who has recently " quantumised " it in the molecular phase hypothesis, a concept also expressed in Bohr's theory of stationary states.

The problem with which we are more immediately concerned is the extent to which magnetic forces enter into and define the behaviour of crystalline substances. This has been investigated by A. E. Oxley,[19] mainly for the case of diamagnetic organic sub-

[18] *Phil. Mag.*, 1920, [vi], **40**, 15 ; *A.*, ii, 460.

[19] *Phil. Trans.*, 1914, [A], **214**, 109 ; 1915, [A], **215**, 79 ; 1920, [A], **220**, 247 ; *A.*, 1914, ii, 424 ; 1915, ii, 219 ; 1920, ii, 351.

stances in which the molecule, not the ion, is regarded as the significant material unit. Oxley's chief contribution to the subject consists in the demonstration that the local molecular field in a diamagnetic substance is comparable in magnitude with the ferromagnetic molecular field, being of the order 10^7 gauss. That this is a field of extremely high intensity is evident when we recall that the most intense field which can be produced artificially is of the order 10^4 gauss. The principal experimental evidence advanced by Oxley is the change in the specific diamagnetic susceptibility (measured in the case of about fifty substances) which accompanies the change from the liquid to the solid state.

On Langevin's theory of magnetism, the molecule of a diamagnetic substance contains oppositely spinning systems of electrons, which counterbalance one another externally, so that the molecule as a whole possesses no initial magnetic moment. When an external magnetic field is applied, the frequency of rotation of one electronic system is increased, whilst the other is diminished, and the molecule becomes slightly polarised and distorted. This small differential effect accounts for the well-known Zeeman effect, and is also the origin of the small magnetic moment possessed by a diamagnetic substance when subjected to a magnetic field. The act of crystallisation can also be regarded as bringing about a similar distortion of the molecule, so that the difference in susceptibility of the solid and liquid forms may be employed to determine the order of magnitude of the local field of magnetic molecular force which gives rise to the rigidity characteristic of the crystalline form.

Let us suppose that ΔM is the change in the moment, M, of an electron orbit produced by applying a magnetic field, H, τ being the period of rotation of the electron (of the order 10^{-15} sec.) and e/m the ratio of the charge to the mass of an electron. Langevin has shown that

$$\frac{\Delta M}{M} = -\frac{H\tau e}{4\pi m} = 10^{-9} \cdot H$$

The strongest magnetic field which can be produced artificially being of the order 10^4 gauss, the largest value of ΔM is $10^{-5}M$. Suppose, however, that, as a result of crystallisation, the molecular field produced is of the order 10^7 gauss, then the value of ΔM is 10^{-2}, which would mean a change of 1 per cent. in the susceptibility. This is the order of the change observed in the case of aromatic compounds. Other evidence confirming the extremely high value ascribed to the molecular field is furnished by the results obtained with double refraction, magneto-striction,

and magneto-rotation. Thus, when a liquid is brought into a magnetic field, it becomes slightly doubly refracting, and at the same time undergoes a small diminution in volume. Oxley shows that if a field of 10^7 gauss could be applied (this being the field which is supposed to be produced by crystallisation), a double refraction comparable with that exhibited by quartz would be produced. Under the same field, the decrease in volume would be about 10 per cent., a value in good agreement with the observed change in volume on crystallisation in numerous cases.

It must be emphasised that, on the view expressed above, the molecule of a diamagnetic substance is locally ferro-magnetic, that is, one part of the molecule is a north-seeking, the other part a south-seeking, pole; this is regarded as the origin of molecular union. The repulsion observed when a diamagnetic substance is placed in a magnetic field is looked upon as purely an induction effect produced in a system of molecules, each of which has initially a zero magnetic moment.

Having considered the intensity, H_c, of the local molecular field, we have now to consider its energy. Let I denote the aggregate local intensity of magnetisation for all the molecules, n, in unit volume. Then $I = ni$, where i is the local magnetic moment of a single molecule. The potential energy E of 1 gram of the substance, in virtue of the grouping and distortion of the molecules constituting the crystalline form (that is, over and above the energy associated with 1 gram of the liquid) is then given by: $E = H_c I/2\rho$, where ρ is the density of the crystal. If we assume that H_c is proportional to I, we can write $H_c = \alpha'_c I$, where α'_c is a constant which Oxley shows is the reciprocal of the limiting local susceptibility of the crystalline medium under a field strength identical with that possessed by the molecular field itself. The energy E can therefore be written as $\alpha'_c I^2/2\rho$, which is analogous to the expression $NI^2/2\rho$ obtained by Weiss for ferro-magnetic substances. The constant α'_c corresponds with N, both having the same physical significance for the respective kind of substance. Oxley shows that the numerical values of α'_c and N are comparable, as are also the I terms, so that the energy of the molecular field in the case of a diamagnetic, crystalline substance is of the same order of magnitude as that of a ferro-magnetic solid, namely, 10^9 ergs per gram. Now in the act of fusion the crystalline form is destroyed; the latent heat of fusion should therefore be of the order $10^9/4 \cdot 2 \times 10^7$, or 25 cal. per gram. The following are a few experimental values:

Benzene .... 30 cal.　Chlorobenzene .. 30 cal.　Aniline .... 21 cal.
Nitrobenzene ... 22 ,,　Naphthalene ... 35 ,,　Pyridine .... 22 ,,

Reference must also be made to the variation in the specific heat

of a crystalline solid as the melting temperature is approached. " In the crystalline state we must regard the molecules as orientated into definite positions with respect to their neighbours by these large intermolecular forces. If at the higher temperatures the molecules undergo rotational vibrations about their mean positions, then it would be expected that the value of I^2 would be somewhat lessened by these vibrations, and we should therefore expect that a small fraction of the energy associated with the grouping would be dissipated as the temperature is raised towards the fusion point. The effect this would have on the variation of the specific heat with temperature would be to add to the normal variation (expressed by Debye's theory) the following positive term:

$$\frac{a'_c}{2\rho J} \cdot I \cdot \frac{\delta I}{\delta T},$$

where T is the absolute temperature and J the mechanical equivalent of the calorie." Nernst and Lindemann have found that close to the melting point there is an abnormal increase in the specific heat of diamagnetic substances, and in order to account for this on the above basis it is necessary to give to I a large value, such as that required by previous considerations. It is necessary to point out that only a small fraction of the energy term E will be dissipated below the fusion point, the major part of it being involved in the act of fusion itself.

Again, the frequency ν of the rotating electrons is given by:

$$\nu = He/2\pi m.$$

If the value ascribed to H be of the order 10^7 gauss, then ν is of the right order of magnitude for an optical frequency. If inside a molecule the intensity were 10^9 gauss, frequencies corresponding with X-rays would be accounted for.

Finally, the intermolecular magnetic field will determine the tensile strength of the crystal, and, as the stresses will be different in general in different directions, planes of cleavage will occur. In this connexion it is important to recall the experiments of Tyndall, who found that the cleavages of diamagnetic substances when placed in a magnetic field stand equatorial, whilst the cleavages of magnetic substances stand axial. Oxley finds in this further evidence that the forces which produce crystallisation are magnetic in nature.

The precise relationship between the electrostatic theory, of atomic and molecular forces as the basis of the crystal lattice and the magnetic theory of the lattice has not as yet been clearly defined. The measure of success which has attended both modes of treatment suggests that they are not mutually contradictory,

although at the present time it is impossible to say more than that in crystals of salts and possibly metals (ionic lattices) the electrostatic forces predominate, whilst in crystals of organic substances (molecular lattices) the intermolecular forces are essentially magnetic.

Ionisation and Resonance Potentials in Gases.

Two types of inelastic encounter between electrons and gaseous atoms are known. One of these in the simplest conditions results in the emission of a single frequency, without ionisation of the gas, whilst the other ionises the gas and causes it to emit a complete spectrum. The potential giving the first kind of encounter is called a resonance potential, that giving the second an ionisation potential. Both types of potential manifest themselves also in connexion with molecules. Thus the process of dissociation of a diatomic gas into neutral atoms would conceivably correspond with the lowest possible resonance potential characteristic of a gas. The importance of measuring such potentials lies in the fact that they afford information regarding the stability of molecules and atoms. We shall consider a number of gases in turn.

Hydrogen.—A very careful investigation of the behaviour of this gas has been carried out,[20] with the following results:

First, there is a weak but appreciable ionisation of the gas at $11 \cdot 5 \pm 0 \cdot 7$ volts. This is ascribed to the ionisation of the molecule, thus: $H_2 \longrightarrow H_2{}^+ + \ominus$ In support of this view it is pointed out that the ion formed at this potential is of molecular and not of atomic dimensions, thereby eliminating the possibility of ascribing the effect to $H \longrightarrow H^{\cdot} + \ominus$, which might be expected to occur at a higher potential. The conclusion drawn in connexion with the potential referred to is a serious criticism of Bohr's theory of the hydrogen molecule, for, according to this theory, the positively charged hydrogen molecule should be incapable of existence. J. J. Thomson, however, has shown that this individual exists in the canal rays.

Secondly, a resonance potential is found at $13 \cdot 6 \pm 0 \cdot 7$ volts. This is ascribed to the dissociation of the molecule into atoms, one of which is normal; the other contains two quanta. The latter emits the first line of the Lyman series in the far ultra-violet. This potential is written by the authors as $(10 \cdot 1 + Q)$ volt, where $Q = 3 \cdot 53 \pm 0 \cdot 25$ volts. This term will be considered later.

Thirdly, a strong ionisation has been observed at $17 \cdot 1 \pm 0 \cdot 27$ volts,

[20] J. Franck, P. Knipping, and T. Krüger, *Ber. Deut. physikal. Ges.*, 1919, **21**, 728; *A.*, ii, 145.

which is written as $(13\cdot5 + Q)$ volts. This is regarded as the ionisation of the hydrogen molecule into an atom, a nucleus, and a free electron, thus: $H_2 \longrightarrow H + H^{\cdot} + \ominus$.

Finally, a new ionisation stage has been observed at the very high voltage $30\cdot4 \pm 0\cdot5$, which is written as $(2 \times 13\cdot5 + Q)$ volts, and corresponds with the most violent change of which the neutral molecule is capable, namely, its ionisation into two nuclei and two free electrons: $H_2 \longrightarrow 2H^{\cdot} + 2\ominus$.

The quantity Q ($3\cdot53$ volts), which occurs in at least three of the observed stages, is ascribed to the dissociation of the hydrogen molecule into neutral atoms. As evidence of the general correctness of this view it is pointed out that $3\cdot53$ volts would correspond with 81,300 cal. per gram-molecule of hydrogen, a quantity which agrees fairly well with the heat of dissociation of the gas, 85,000 cals. as determined by Langmuir. This resonance potential was not observed directly by the authors named, although presumably it was looked for. It is of interest in this connexion to note that Mohler and Foote [21] obtained "evidence of a slight resonance collision between $2\cdot5$ and $3\cdot5$ volts, but the value has not yet been accurately fixed." It may perhaps be pointed out that by subtracting stage 3 from the final stage referred to we obtain the value $13\cdot3$ volts as the ionisation potential of the hydrogen atom, namely, $H \longrightarrow H^{\cdot} + \ominus$.

Values differing apparently from those of Franck, Knipping, and Krüger have been obtained by other workers. Thus, Franck and Hertz, Bishop, Davis and Goucher, found somewhat earlier that ionisation sets in at a potential of about 11 volts, and the latter authors further found a second ionisation potential at $15\cdot8$ volts. This value, which does not find any counterpart in the work of Franck, Knipping, and Krüger, is accounted for by assuming that the hydrogen atom has an affinity for an electron, so that the energy of decomposing the negatively charged ion, according to the scheme $H' \longrightarrow H + \ominus$, is $2\cdot2$ volts, where $2\cdot2 = (15\cdot8 - 13\cdot6)$ volts.

Hydrogen has also been carefully investigated,[22] with the following results:

First, there is a radiation or resonance potential at a minimum electron velocity equivalent to $10\cdot5$ volts. This is presumably the same as the $10\cdot1$ volts inferred by Franck and his collaborators as a possible resonance potential of the molecule. Horton ascribes this effect to radiation from the atom by displacement of an electron from one orbit to another.

[21] *J. Opt. Soc. Amer.*, 1920, 4, 49 ; *A.*, ii, 464.

[22] F. Horton and (Miss) A. C. Davies, *Proc. Roy. Soc.*, 1920, [A], 97, 23 ; *A.*, ii, 215.

Secondly, a further type of radiation potential is produced at 13·9 volts. Horton ascribes this to radiation from the molecule. This is presumably the same as the resonance potential observed by Franck and his co-workers at 13·6 volts.

Thirdly, Horton and Miss Davies find that ionisation of the gas occurs at 14·4 volts. This value does not appear to correspond with any found by the other workers. It is rather a striking fact, however, that 14·4 volts corresponds with the wave-length 84 $\mu\mu$, which lies very near to the accepted value of the dispersional wave-length, 86 to 87 $\mu\mu$, obtained from refractive index data. Horton ascribes this stage to the ionisation of the atom $H \longrightarrow H^{\cdot} + \ominus$ It will be recalled that the value calculated for this process on Franck's data is 13·3 volts, which agrees well with the value calculated by Bohr.

Finally, Mohler and Foote [21] find a resonance potential at 10·4 volts, which agrees very well with the first stage observed by Horton and Miss Davies. Mohler and Foote also find a first ionisation stage at 13·3 volts, which they ascribe to ionisation of the atom, in excellent agreement with the value calculated above. These authors also find a second ionisation at 16·5 volts, which they ascribe to the molecule. This evidently is intended to correspond with the value 17·1 volts found by Franck and his co-workers.

On the whole, the various observations are rather discordant. Something like order may be obtained from the various results if we take as our starting point the value 3·5 volts or 81,300 cal. for the dissociation of the molecule into neutral atoms, and assume that the various stages are approximately even multiples of this quantity. The various potentials and the corresponding wave-lengths calculated on this basis are compared with the observed values in the table on p. 16.
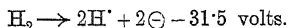
These various stages are logically connected with one another. For example, stage (6) follows from stages (1) and (4). Thus, from process (4) we have:

$$2H \longrightarrow 2H^{\cdot} + 2\odot - (2 \times 14) \text{ volts},$$

and from (1):

$$H_2 \longrightarrow 2H(\text{normal atoms}) - 3\cdot5 \text{ volts},$$

whence

$$H_2 \longrightarrow 2H^{\cdot} + 2\ominus - 31\cdot5 \text{ volts}.$$
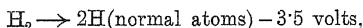
Stage (6) would appear to be the highest possible stage of activation of which the neutral molecule is capable. The corresponding wave-length is much shorter than the limit ascribed to the hydrogen spectrum by Richardson and Bazzoni. It is obvious that the potentials of hydrogen require further exact investigation.

Process number.	Nature of process.	Potential calculated, volts.	Wave-length in $\mu\mu$.	Potential observed.
1.	$H_2 \longrightarrow 2H$. Both atoms normal. Resonance.	$3\cdot5 = (3\cdot5 \times 1)$	348	2·5 to 3·5
2.	$H_2 \longrightarrow 2H$. One atom normal, the others with displaced electron. Resonance.	$7\cdot0 = (3\cdot5 \times 2)$	174	not observed
3.	$H_2 \longrightarrow 2H$. Both atoms with displaced electrons. Resonance.	$10\cdot5 = (3\cdot5 \times 3)$	116	10·1 10·4 10·5
4.	$H \longrightarrow H^{\cdot} + \ominus$. Ionisation of the atom.	$14\cdot0 = (3\cdot5 \times 4)$	87 (dispersional wavelength)	13·3 14·4
5.	$H_2 \longrightarrow H + H^{\cdot} + \ominus$. Ionisation of the molecule. The atom is normal.	$17\cdot5 = (3\cdot5 \times 5)$	69·6	16·5 16·9 17·1
6.	$H_2 \longrightarrow 2H^{\cdot} + 2\ominus$. Complete ionisation of the molecule.	$31\cdot5 = (3\cdot5 \times 9)$	38·7	30·4

Nitrogen.—The relatively early experiments of Franck and Hertz led to the value 7·5 volts as the ionisation potential of nitrogen In view of the great chemical stability of the molecule this value is surprisingly low. B. Davis and F. S. Goucher [23] showed later that this potential did not give rise to ionisation, but to resonance. They found a more intense type of resonance potential at 9 volts and a true ionisation at about 18 volts. H. D. Smyth [24] has investigated the values of the lower potentials with the following results:

First, there is a marked · production of radiation (resonance) at $8\cdot29\pm0\cdot04$ volts. Secondly, there is a doubtful effect which he con siders may be due to silicon at 7·3 volts; and thirdly, an effect at 6·29 volts, which only appears at low pressures, and which he finally attributes to nitrous oxide as an impurity. Smyth has also obtained qualitative evidence in support of Davis and Goucher's value 18 volts, for the ionisation potential. Smyth concludes that the resonance potential at 8·29 volts corresponds with the dissociation of the nitrogen molecule into neutral atoms. The effective wave length is therefore 149 $\mu\mu$, and the heat of dissociation per gram molecule 190,000 cal. Mohler and Foote [21] confirm the general cor rectness of previous determinations by finding a resonance potential at $8\cdot18\pm0\cdot10$ volts and an ionisation potential at $16\cdot9\pm0\cdot5$ volts. ·

Oxygen.—The value hitherto accepted for the ionisation potential of this gas has been about 9 volts. Mohler and Foote [21] have carried out a careful revision, and find a resonance potential at

7·91±0·1 volts, which corresponds with the known wave-length 1570 Å. They also find an ionisation potential at 15·5±0·5 volts, which agrees fairly well with the potential 15·2 volts calculated from the dispersional frequency of oxygen. It might be suggested that the value 9 volts corresponds with the process $O_2 \longrightarrow O_2^{\cdot} + \ominus$ analogous to the hydrogen potential 11·5 volts, $H_2 \longrightarrow H_2^{\cdot} + \ominus$, which lies between the resonance and true ionisation potential of this gas.

Iodine Vapour.—The behaviour of iodine vapour in respect of fluorescence, ionisation, and dissociation into neutral · atoms has been examined by K. T. Compton and H. D. Smyth.[25] They point out that the fluorescence of gases and vapours is not generally accompanied by ionisation, and that therefore fluorescence is due to a shift of an electron from a position of high to one of low potential energy, a view first expressed in somewhat general terms by Baly as an alteration in the degree of openness of the molecular field of force. Compton and Smyth have obtained experimental evidence of the correctness of this view from measurements of the minimum energy required to ionise a fluorescing molecule. The normal molecule requires 10 volts, the fluorescing molecule 7·5 volts when excited by the green mercury line. The difference, 2·5 volts, corresponds with the quantum of energy of the mercury line as calculated by the relation $Ve = h\nu$. This result is direct experimental evidence of the existence of molecules with an abnormal energy content; such molecules are, in fact, partly active in respect of ionisation. Turning to the relationship between ionisation and dissociation into atoms, Compton and Smyth find two types of ionisation in iodine vapour, namely, a very weak ionisation at 8·5 volts, which they attribute to the ionisation of the free iodine atoms (formed in sensible quantity by contact with the hot filament), and also a very intense ionisation at 10 volts attributed to the molecules. The difference, 1·5 volts, should correspond with the energy required to dissociate a molecule of iodine into neutral atoms. This value, when converted into cals per gram-molecule, agrees closely with the known heat of dissociation. This result, it may be pointed out, also substantiates the view that the nascent atoms require no energy of activation in respect of their recombination. The wave-length corresponding with the above voltage (1·5) is about 820 $\mu\mu$. Iodine vapour would therefore be expected to exhibit an absorption band in this region; it does not appear to have been looked for hitherto.

Helium.—The potentials of this gas will be considered in the next section.

Neon.—The minimum radiation (resonance) potential has been

found [26] to be 11·8 volts, the minimum ionisation potential 16·7 volts. A second resonance potential has also been found at 17·8 volts, and a second and third ionisation potential at 20·0 and 22·8 volts respectively. The existence of three ionisation potentials and two critical resonance potentials indicates that neon differs more from helium and argon than would have been anticipated. On the usual view the resonance and ionisation potentials correspond respectively with the lowest and highest frequencies of some particular series. It would be expected, therefore, that there should be as many resonance potentials as there are ionisation values. The fact that only two resonance potentials were found in this gas is ascribed to the possibility that two lie very close together, in which case one might escape detection. Another possibility is that the ionisation observed at one of the three potentials is a spurious effect. The resonance potential, 11·8 volts, appears to be associated with the ionisation potential, 16·7 volts, and the resonance potential at 17·8 volts with the ionisation at 22·8 volts. If neon consists of two or more constituents having different radiation and ionisation potentials, the critical potentials, 11·8 and 16·7, are attributed to one isotope, the values 17·8 and 22·8 to the other.

Argon.—Horton and Miss Davies [27] have also investigated this gas very carefully. Their final conclusions are that argon exhibits a resonance potential at 11·5 volts and an ionisation potential at 15·1 volts. The latter corresponds with the wave-length 817 Å. Lyman has found that the limiting wave-length of the argon spectrum lies very close to 800 Å. The agreement between the two results is satisfactory.

As regards the resonance and ionisation potentials of metallic vapours, a considerable amount of research has been carried out. One of the chief difficulties is that of the minimum arcing potential and the potential required to maintain the arc. In general, it may be said that the ionisation potential corresponds with the convergence frequency of a series, which, however, is not necessarily the principal series. Another point in dispute is as to whether the resonance potential corresponds with a single line or not. Until more general agreement is attained among the workers in this field as to the interpretation of their results there is little advantage in attempting to summarise them.

Before leaving the subject of ionisation of gases it may be pointed out that in the case of diatomic molecules two distinct types of ionisation may be expected. In the first the molecule parts with an electron, but preserves its general molecular structure. This is

[26] F. Horton and (Miss) A. C. Davies, *Proc. Roy. Soc.*, 1920, [A], **98**, 124 ; *A.*, ii, 657.   [27] *Ibid.*, **97**, 1 ; *A.*, ii, 215.

the type of ionisation met with in the diatomic gases referred to above. "It seems probable that materials capable of ionising in this manner should possess a characteristic spectrum." [28] In the second type of ionisation the molecule breaks up directly into a positive and a negative ion. (Naturally, the first type of ionisation, in so far as it affects atoms, will ultimately, in certain cases, give rise to the same end-products as those obtained in a single step during the second type of ionisation) The second type of ionisation is met with in the case of hydrogen chloride, already discussed in the first section of this Report. "Materials which are ionised in this manner probably do not possess characteristic spectra in the ordinary sense," beyond the line in the far ultra-violet corresponding with the union of the two ions. It may be anticipated that the alkali haloids in the state of vapour exhibit the second type of ionisation. This would explain the known absence of any emission spectrum characteristic of the salt. We would expect instead to observe the spectrum of the alkali metal produced by a recombination of the metallic ions with electrons. Further, the flame emission spectrum characteristic of the metals is suppressed by an excess of halogen. This finds a simple explanation on the basis that the excess of halogen in the flame ultimately gives rise to halogen ions in relatively large amount with which the metallic ions combine rather than with the electrons.

The Atomic Model of Bohr and the Structure of the Helium Atom.

One of the main objections to Bohr's theory of the structure of a molecule such as that of hydrogen is that it requires the hydrogen molecule to be paramagnetic, whilst it is, in fact, diamagnetic. An attempt has been made [29] to reconcile Bohr's theory with the actual diamagnetism of hydrogen on the basis of rotations and vibrations as well as of translatory movement of the molecule, so that although the structure is inherently paramagnetic the gas would behave as though diamagnetic. The plausibility of this explanation has been adversely criticised by Oxley [30] in the light of recent experimental data, and the conclusion is drawn that thermal oscillations and rotations have little to do with the origin of diamagnetism, and that, in fact, the Bohr model for the molecule is incorrect. Oxley concludes that the free hydrogen atom is probably paramagnetic, but that the structure of the molecule must be such that by compensation of electronic rotations it is as a whole diamagnetic. A

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[28] P. D. Foote and F. L. Mohler, *J. Washington Acad. Sci.*, 1920, **10**, 435 ; *A.*, ii, 666.

[29] J. R. Ashworth, *Nature*, 1920, **105**, 516.   [30] *Ibid.*, 581.

diagrammatic representation of such a model was already given by Oxley.[31]

A further criticism of Bohr's theory of the hydrogen molecule is that it leads to a value for the heat of dissociation of the gas into neutral atoms which is too low, namely, 60,000 cal. per gram-molecule, the best observed value being 85,000 cal. The mechanism of this dissociation has been considered in some detail by M. Planck.[32] This quantity at sufficiently low temperatures is necessarily equal to the difference between the energy of the molecule and that of the two atoms Planck discusses three different modes of dissociation. On the first it is assumed that the electrons in atoms and in the molecules describe circular orbits with single quanta; on this basis, which is Bohr's original basis, the heat of dissociation is found to be 62,100 cal. On the second assumption, that in all the atoms and molecules those electronic orbits which possess less than one quantum are correspondingly probable, the heat of dissociation on the basis of the classical mechanics is infinite; on the theory of relativity it becomes 570,000 cal., a quantity which is much too great. The third assumption is that in addition to circular orbits the electrons perform pendulum movements; this leads to the much better value, 140,000 cal. Planck concludes that the assumption of circular orbits is not justified. Sommerfeld somewhat earlier had considered elliptical orbits, and had applied the principal of relativity to these in order to explain the fine line spectrum.

Attention has already been drawn to a further discrepancy between Bohr's theory and experiment, namely, the existence of positively charged hydrogen molecules as indicated by the work of Franck, Knipping, and Krüger. It has also been shown by Born (compare section on the energetics of the crystal lattice) that Bohr's theory is inapplicable to crystals.

Finally, a brief reference may be made to the work of L. Schames.[33] It is known that the moment of inertia of a molecule can be calculated from the chemical constant of the substance. Assuming the molecule to be a di-pole, it is possible to obtain the distance between the two charges from the moment of inertia, and from this, in turn, to calculate the electric moment by applying the quantum theory. Using the ring electron structure and carrying out these calculations for the case of water-vapour and carbon dioxide, Schames has obtained values for the electric moment which are much greater than those obtained by Jona on the basis of Debye's theory from the temperature-coefficient of the dielectric

[31] *Nature*, 1920, **105**, 327.

[32] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 914 ; *A.*, ii, 423.

[33] *Physikal. Zeitsch.*, 1920, **21**, 156 ; *A.*, ii, 301.

capacity of the gas. The discrepancy suggests that the electrons are not arranged in a ring round the nucleus, but in some spatial arrangement, such as that given by the G. N. Lewis cubical atom model.

We now turn to the problem of the structure of the helium atom. On the theory of Bohr the helium atom is regarded as consisting of a nucleus carrying two positive charges with two electrons rotating in the same direction and in the same orbit around the nucleus. On this basis Bohr calculated the ionisation potential of helium to be 28·8 volts. The value actually found [34] is 25·0 volts in very pure helium, a result in good agreement with earlier measurements,[35] namely, 25·4±0·25 volts. Whilst Bohr's theory, as already pointed out, appears to be exact for the simple case of an atom having one electron, that is, for the hydrogen atom and the positively charged helium atom, the discrepancy between the observed and calculated values of the ionisation potential of the neutral helium atom is sufficiently great to cast serious doubt upon the correctness of the model suggested by Bohr for this case and for all other cases involving more than one electron.

In connexion with helium, I. Langmuir [36] has shown recently that the experimental value may be accounted for by attributing to the electrons a type of motion first suggested by Landé in connexion with crystals—already considered in a previous section—in which the electrons do not complete a circular or elliptic orbit, but at a certain stage are made to retrace their path, owing to the repulsion of a neighbouring electron. The helium atom, as envisaged by Langmuir, consists of the nucleus and the two electrons lying in the same plane, the electrons being placed symmetrically with respect to the nucleus. The electrons move with equal velocities in this plane, one in a clockwise the other in an anti-clockwise direction. If there were no forces of repulsion between the two electrons, and if suitable velocities were chosen, the electrons would move in a single circular orbit about the nucleus, but in opposite directions. That is, they would pass through one another twice in each completed rotation. Owing to their mutual repulsion, however, as they approach one another, their velocity may be reduced to zero, and with suitable choice of velocity they may be made to retrace their path when only a part of the orbit has been traversed. In fact, they never cross a line drawn through the nucleus at right angles to the line joining the nucleus and electrons when the latter

[34] F. Horton and (Miss) D. Bailey, *Phil. Mag.*, 1920, [vi], **40**, 440; *A.*, ii, 660.

[35] J. Franck and P. Knipping, *Physikal. Zeitsch.*, 1919, **20**, 481; *A.*, ii, 72.

[36] *Science*, 1920, **51**, 605; *A.*, ii, 656.

are farthest apart. Langmuir has calculated that the path of each electron is very nearly an arc of an eccentric circle extending 77° 58' each way from the mid-point of swing, as measured from the nucleus. The movement of each electron is analogous to the movement of a pendulum bob in which the string is somewhat lengthened as the bob swings towards its position of maximum potential energy. Applying the quantum theory, Langmuir finds that the radius vector for the electron at its mid-point is $0·2534 \times 10^{-8}$ cm., which is roughly four-fifths of the radius of the completed orbit in Bohr's model. Even at the end of the swing the calculated radius ($0·2882 \times 10^{-8}$ cm.) is slightly less than that calculated by Bohr. The number of complete " oscillations " per second is 1·22 times the number of "revolutions" of the Bohr electrons. Finally, the ionisation potential calculated on the new type of motion and structure is 25·59 volts, which agrees reasonably well with the observed value. Not only is the ionisation potential accounted for in a much more satisfactory manner than it is on the Bohr model, but, by restricting the movement of the electrons to certain portions of the sphere surrounding the nucleus, as is done in the above model, we are obviously approximating to the conditions represented in the well-known octet theory of atomic structure, which in the hands of Langmuir has been shown to be the most satisfactory one from the chemical point of view.

The Mobility of Electrolytic Ions

Attempts [37] have been made in recent years to account for the observed velocity of ions in a field of electric force by applying Stokes's well-known expression. According to this expression, the velocity should vary inversely as the radius of the ion. Whilst this conclusion is borne out more or less exactly by a considerable number of large and heavy ions, it is not borne out in the case of simple ions, especially those of the alkali metals. Thus the atomic volumes of the alkali metals increase from lithium to cæsium, and it can scarcely be doubted that the corresponding ions follow the same sequence. That is, the lithium ion should travel most rapidly, the cæsium least rapidly; this, however, is the reverse of what is found.

The difficulty has been explained on the familiar assumption of hydration, this term being employed to denote one or more definite stoicheiometric compounds of ion and water molecules. The

[37] R. Lorenz, Zeitsch. anorg. Chem., 1919, **105**, 175; A., 1919, ii, 212; R. Lorenz and I. Posen, ibid., 1916, **94**, 265; A., 1916, ii, 312; R. Lorenz, Zeitsch. Elektrochem., 1920, **26**, 424; A., ii, 729.

smaller the actual magnitude of the ion, the more intense is the electric field at its surface, and consequently the greater the tendency to attach water molecules. The latter process has been subjected to a fairly rigorous treatment by Born,[38] commencing with the idea that definite hydrates are not necessarily formed, but that, instead, a certain degree of condensation or compression of the water molecules occurs in the immediate neighbourhood of each ion, a water molecule being regarded as an electric di-pole [39] of known moment. A number of the water molecules, in virtue of their polarity, orientate themselves in a certain way with respect to the ion. When the latter is set in motion, the water molecules are dragged along with it, and so slow down the speed of the ion, each di-pole suffering at the same time a certain amount of torsion. These effects have been allowed for by Born in making use of Stokes's expression in its usual form, in which, however, an "apparent radius" term, r', is substituted for the actual radius, r. The relation between r and r' is given by the expression

$$r' = r\left(1 + \tfrac{1}{3}\left(\frac{r_0}{r}\right)^4\right),$$

where r_0 is a constant, called the characteristic radius, and is defined by

$$r_0 = \sqrt{\frac{anFM}{RT}},$$

in which F is the faraday, M the moment of the di-polar water molecule, R the gas constant, T the absolute temperature, n the valency of the ion, and a a quantity, the maximum value of which is unity, the minimum value being $1/\epsilon$, where ϵ is the dielectric capacity of the medium. The expression for r' (that is, the value which must be inserted in Stokes's expression in order to account for the observed velocity) becomes identical with the actual radius r for large ions. As we pass to a consideration of smaller ions, the value of r' falls to a minimum, given by $\tfrac{4}{3}r_0$, and then rises rapidly as r itself further falls, so that for very small ions the value of r' is decidedly greater than r.

A preliminary test of the validity of the expression for r' consists in showing that r_0 has the proper atomic dimensions. Inserting the usual values for n, F, R, T, and the value $M = 1.87 \times 10^{-18}$ e.s.u., as determined by M. Jona,[40] it is found that $r_0 = 1.47\sqrt{a}$. Since a varies between 1 and $1/81$ for water, the value of r_0 lies

[38] Zeitsch. Elektrochem., 1920, 26, 401.

[39] Compare P. Debye, Physikal. Zeitsch., 1912, 13, 97 ; Ber. Deut. physikal. Ges., 1913, 15, 777.

[40] Physikal. Zeitsch., 1919, 20, 14 ; A., 1919, ii, 130.

between 10^{-7} and 10^{-8} cm.; that is, it is of the right order of magnitude.

The equation connecting r' and r can be applied quantitatively to the case of ions by assuming that the cæsium ion corresponds more or less exactly with the minimum value of the apparent radius, that is, $r'_{cs} = \frac{4}{5}r_0$. The apparent radius for this ion is found experimentally to be 1.11×10^{-8} cm. Hence

$$r_0 = 0.833 \times 10^{-8} \text{ cm.}$$

Employing this value, Born finds the following values of r and r' for a number of univalent ions:

Ion	Cs.	Rb.	K.	Na.	Li.	I.	Br.	Cl.
Apparent radius $(r' \times 10^8)$	1.11	1.12	1.17	1.74	2.26	1.13	1.12	1.15
True radius $(r \times 10^8)$	0.83	0.77	0.69	0.51	0.45	0.95	$\begin{cases} 0.77 \\ 0.92 \end{cases}$	0.73

The true radius is that calculated from the apparent radius by means of the equation first mentioned. The conclusion to be drawn is that in the case of the alkali ions, although the apparent radius increases as we pass from cæsium to lithium, this is not incompatible with the fact that the true radius diminishes. The discrepancy referred to at the beginning of this section is thus explained. It may be pointed out, however, that Born's theory, although satisfactory, cannot be regarded as numerically exact, owing to the doubt which exists in connexion with the value of α. Numerical values can only be obtained at the present time by making an assumption, necessarily somewhat in error, in connexion with the magnitude of the apparent radius of the cæsium ion.

Electrical Conductivity of Solid and Fused Salts.

In the Report for 1918 reference was made to the work of J. C. Ghosh on the anomaly of strong electrolytes, in which Milner's concept of complete ionisation at all dilutions was employed to account for the observed conductivity. The lattice theory of crystalline salts, reviewed in the first section of the present Report, involves, obviously, a structure analogous to that of complete ionisation. Ghosh[41] has applied his former method of treatment to the case of solid salts, pointing out that although ionisation is complete, the ions are not free to move until very high temperatures are attained. The number of free ions in the case of a uni-univalent salt is then given by

$$2n = 2Ne^{-W/2RT} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N is the Avogadro constant and W is the work which must

be done at temperature T by the ions of 1 gram-molecule to overcome the elastic forces to which they are ordinarily subjected. It follows that the specific conductivity, μ, of a solid salt is expressed by the relation

$$\mu = \frac{U}{v} 2Ne^{-W/2RT} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where v is the molecular volume of the salt and U the average mobility of the ions at the temperature T.

Ghosh considers that the variation of W with temperature may be obtained by an application of Nernst's heat theorem, the system being a condensed one, thus:

$$W = W_0 + \beta T^2.$$

The magnitude of W depends on the purely local forces at a point inside the solid, and may be regarded as running parallel with the elastic rigidity. Since the latter diminishes as the temperature rises, W will diminish, and consequently β is a negative quantity. At the melting point, T_m, where the purely local part of the forces is negligible, Ghosh assumes

$$W = W_0 + \beta T_m{}^2 = 0.$$

β can thus be expressed in terms of W_0, so that, finally, we have

$$W = W_0\left(1 - \frac{T^2}{T_m{}^2}\right) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The variation of the mobility, U, of an ion in a solid with rise in temperature is accounted for in a way analogous to the former electron theory of metallic conductors. This leads, finally, to the expression

$$U = \text{constant}/\sqrt{T} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

On combining (2), (3), and (4), we obtain

$$\frac{W_0(T_2 - T_1)}{2R}\left\{\frac{1}{T_1 T_2} - \frac{1}{T_m{}^2}\right\} = \log_e \frac{\mu_2 \sqrt{T_2}}{\mu_1 \sqrt{T_1}} \quad . \quad . \quad . \quad (5)$$

This expression contains only one unknown constant, W_0, which can be easily obtained from any two observed values of μ. On comparing the observed specific conductivities of solid salts with the values calculated by means of equation (5), satisfactory agreement is obtained. By way of illustration, the results obtained in the case of sodium chloride are quoted in the following table, the final column of which contains the activity-coefficient, a,[42] calculated from equation (1), namely,

$$\frac{W}{2RT} = \log_e \frac{2N}{2n} = \log_e \frac{1}{a}.$$

[42] Compare *Ann. Reports*, 1917, **14**, 11.

Sodium Chloride.

$W_0 = 51 \cdot 2$ kilo.-cal. $T_m = 1083$ abs.

T abs.	μ calcd. $\times 10^6$.	μ observed $\times 10^6$.	a.
903	—	12·6	0·0127
923	21·2	21·2	0·0216
943	35·4	35·0	0·0363
983	91·0	95·0	0·0988
1023	240·0	240·0	0·2551
1073	729·0	729·0	0·803 4

It may perhaps be pointed out that the values obtained by Ghosh for W_0 are very similar to the latent heat of sublimation at absolute zero calculated by Haber and Reis (compare first section of this Report). One would rather have expected W_0 to be analogous to a latent heat of fusion, the W term by definition representing a free energy change, the latent heat representing an internal energy term.

It follows from equation (3) above that at the melting point all the ions are free to move past one another, since W is zero at this temperature, and consequently the activity-coefficient as defined above becomes unity for fused salts [compare equation (1)]. Hence the specific conductivity of fused salts does not vary with the temperature in a logarithmic manner. This is to be expected, as all the ions present contribute to the conductivity. The latter is thus found, in agreement with experiment, to vary linearly with the temperature, such variation being due entirely to a change in the mobility of the ions.

<div style="text-align: right">W. C. McC. LEWIS.</div>

INORGANIC CHEMISTRY.

MANY papers have been published on orthodox inorganic chemistry during the last year, and several of these awaken more than a passing interest. There have appeared, however, four papers by Aston, Rutherford, Harkins, and Wendt and Landauer, which outshine all others in importance, for without question they bid fair to revolutionise the fundamental conceptions of chemistry. Whilst by some the signs of the impending change have been recognised, the majority of chemists must now awaken to the fact that a new philosophy is being born. The brilliant discoveries of Soddy and Fajans of the existence of isotopes mark the first real step after the discovery of the production of helium in the radioactive disintegration of atoms. About the same time Thomson, Collie, Patterson, and Masson stated that helium and neon are produced in hydrogen-filled vacuum tubes under the influence of a powerful electric discharge. Very soon afterwards appeared the Harkins theory that all elementary atoms are built up either of helium atoms or of atoms of helium and hydrogen. Last year the next step was gained when Rutherford succeeded in disrupting the atom of nitrogen.

It may now be said that the whole story is practically complete, and a wonderful story does it prove to be. Perhaps the most startling of all the new knowledge gained is that on the oxygen standard all atomic weights, with the exception of hydrogen, are exact whole numbers, and that the fractional values we have accepted as the result of highly accurate work are merely fortuitous statistical averages due to a mixture of two or more isotopes. Whilst this has been proved by experiment, it also is a necessary corollary of the theories of atomic structure. In the annual Report for 1917 reference was made to Harkins' theory that all elementary atoms are built up of helium atoms or helium and hydrogen atoms. This theory has now been published in its complete form, and it carries conviction in its train. An essential feature is that the hydrogen isotope H_3 plays an integral part in atomic structure, that it has a definite power of existence, and that very probably it is

identical with the nebular material called nebulium.   First de-
tected by Thomson, then more fully confirmed by Aston, H_3 has
now been prepared from hydrogen.

Then, again, Rutherford has shown that by the disruption of the
atoms of oxygen and nitrogen an element of mass 3 is produced,
which, however, is an isotope of helium.   Rutherford considers that
the atom of mass 3 which enters into the nuclear structure of atoms
is this helium isotope and not H_3 as Harkins assumes.

Whichever view may prove to be correct, there can now be little
doubt that all elementary atoms are built up from helium or from
helium and atoms of mass 3, and, moreover, it is accepted by the
new school that helium itself is built up from four atoms of hydro-
gen.   The added importance of Collie's work on the formation of
helium and neon in hydrogen-filled vacuum tubes is manifest, for
it has now become an obvious result from the new theories.

Another most interesting aspect of this new knowledge is that
the synthetic process whereby our elements are known to be
produced during the life history of the stars from the original
nebulium by way of hydrogen and helium can now be understood.

It is difficult to write of these discoveries and theories in a calm
and measured fashion.   They are so great in their achievement, so
stupendous in their meaning, and so subversive in their effect that
some enthusiasm may perhaps be allowed to him who records them.
Strange it is that after all these years the old hypothesis of Prout
should rise triumphant, for, in a word, it is this that has occurred.
In the Report for 1914, when the discovery of isotopes and Collie's
work had been announced, the writer ventured to write the follow-
ing words: "As did his forefathers of pre-Avogadro days, so also
does he (the chemist of to-day) now await that great generalisation
which shall co-ordinate and link up all the threads to found a new
philosophy.   Radioactivity, enhanced line spectra, the intra-stellar
elements, active nitrogen and oxygen, atomic disintegration,
atomic-weight variation, all will be unified and embodied in the
new philosophy of the twentieth century.   Then will a new chem-
istry in its greater meaning emerge as a phœnix from the glowing
parental fires of the many chemistries of to-day."

Little apology is needed for making this quotation, since the
prophecy seems to be almost complete in its fulfilment.

Atomic Theory.

In the Reports for 1913 and 1914 reference was made to the work
of Thomson, of Collie and Patterson, and of Masson on the pro-
duction of helium and neon from hydrogen at low pressures under

the influence of the electric discharge. Negative results were recorded by Strutt and by Merton, but Collie, using Merton's own apparatus, obtained definite evidence of the formation of both these gases. Some further experiments have been carried out during this year, and once more negative results have been obtained.[1] In view of the fact that Collie himself more than once obtained negative results when using different induction coils, the writer suggested that the explanation of the divergence of the results obtained by different observers is to be found in the fact that a particular type of discharge is necessary. Piutti and Cardoso, whilst admitting that our rudimentary knowledge does not permit us to discuss this explanation, point out that their results strengthen the probability against it. They say that as in the somewhat analogous case of active nitrogen, where considerable divergence of opinion existed, it would be advisable that joint work be carried out systematically in order definitely to settle this important question.

There is little doubt that the trend of recent ideas will create less antagonism to the formation of helium and neon in vacuum tubes than was the case six years ago. The work of Rutherford on the disintegration of nitrogen and oxygen atoms has undermined the old confidence in the immutability of the atom. On the other hand, all other experimental work has been in the direction of the disruption of atomic nuclei, whilst Collie's work means a synthesis of atomic nuclei heavier than the parent hydrogen.

There can be no question that one of the most complete theories advanced as regards the structure of atomic nuclei is that by Harkins.[2] His earlier papers were reviewed in the Report for 1917. According to this theory, the elements are of two kinds, namely, those of even atomic number, the atomic nuclei of which are composed of helium nuclei alone, or helium nuclei together with cementing electrons, and those of odd atomic number, the nuclei of which are composed of helium and hydrogen nuclei together with cementing electrons. Further, the helium nucleus consists of four hydrogen nuclei, together with two cementing electrons, the loss of mass being due to the packing effect. The helium nucleus is the most stable configuration of all, whilst next in order of stability comes the group of atoms or even atomic number. An interesting fact arises in connexion with the number of hydrogen nuclei which are associated with the helium nuclei in the second class of elements. In the case of the lighter elements with odd atomic number this number is always three save in the exceptional case of nitrogen,

[1] A. Piutti and E. Cardoso, *J. Chim. phys.*, 1920, **18**, 81 ; *A.*, ii, 311.
[2] W. D. Harkins, *Physical Rev.*, 1920, **15**, 73 ; *A.*, ii, 479.

where it is two. The extremely frequent occurrence of this group
of three hydrogen nuclei suggests that it probably occurs alone as a
unit with a nuclear charge equal to 1 and atomic weight of 3, and
therefore structurally it will be an isotope of hydrogen. If the
hypothetic nebulium exists at all it is probably this form of hydro-
gen, and it is interesting that from a study of the Döppler effect
the atomic weight of this element has been found to be about 3.[3]

Now there is one point in connexion with the Harkins theory
which requires consideration. If, for example, the elements with
even atomic numbers are formed from helium nuclei, why is it that
they are not more unstable in view of the fact that the helium
atom is the most stable form? It would seem necessary to con-
clude that the elements are metastable, and that they are able to
exist owing to their possessing an external force field. If this is
broken by the supply of energy, then the atomic nucleus will
become unstable. If this principle of external fields is accepted,
then it only becomes a question of supplying the right amount of
energy to the hydrogen atom for the association to become possible
of three or four nuclei to form H_3 or helium. On the Harkins
theory, therefore, there is no reason against the production of H_3
and helium in vacuum tubes from hydrogen if the discharge em-
ployed produces the suitable type of energy. Indeed, such a
phenomenon is rather to be expected than denied in view of the
stability of the helium nucleus. The writer is therefore all the
more encouraged to insist on the correctness of his suggestion made
in 1914 that the contradictory results obtained by Thomson, Collie,
Patterson, and Masson on the one hand, and by Strutt, Piutti and
Cardoso on the other, are due to the absence of sufficient energy of
the right kind in the latter and negative experiments. There are
two alternative possibilities as to the nature of the energy required
to break open the fields of the hydrogen atom. It may either be
radiant energy of short wave-length or it may be energy given by
rapidly moving particles. The production of either of these in a
given vacuum tube varies remarkably with the conditions. The
importance of this work has undoubtedly increased, and it is a
matter of some moment that the question as to the production of
helium from hydrogen be decided.

Reference may here be made to a branch of investigation which,
although not chemical, must possess great interest for the inorganic
chemist, namely, stellar development. According to the modern
views of astro-physicists there is little doubt that in the stars a
development process is taking place whereby the chemical elements
are being synthesised from hydrogen and helium as parents. Now

[3] C. Fabry and H. Buisson, *Astrophys. J.*, 1914, **40**, 256.

it would seem fairly certain from a study of the spectra and rotational velocities of certain nebulæ, particularly the one in Orion, that the original material from which the synthetic process starts is nebulium, which as the first stage in the process forms hydrogen and helium. When it was discovered that the probable atomic weight of this gas is 3, it appeared somewhat incomprehensible that a synthetic process should give both hydrogen and helium. In all probability, on the basis of Harkins' theory that nebulium is H_3 the first stage is the formation of hydrogen, which then associates to give helium, which in its turn associates to give elements of even atomic numbers. If this is so, by far the greatest amount of condensation will take place in the direction of the elements of even atomic numbers. The great predominance of elements of this class has been pointed out by Harkins, who offers two explanations of the relative scarcity of the elements with odd atomic numbers which consist of helium and H_3 atoms. First, their scarcity may be due to their relative instability, and secondly, there may have been present during the synthetic process relatively little H_3. The first alternative is unsatisfactory, for at present there seems little, if any, direct evidence that the elements of odd atomic numbers are less stable than their fellows. The second alternative fits in very well with the present suggestion, since, if the first stage is the production of hydrogen from H_3, and the second stage is the formation of helium from the hydrogen, it is probable that in any later association there will be present only small amounts of H_3. The Harkins theory would therefore fill an undoubted gap in the theories of stellar development.

An important paper has appeared during the year on the mass spectra, or positive ray spectra, of the elements by Aston, who describes his apparatus in detail and the most recent results he has obtained.[4] The principle of the method consists in producing the positive rays with a given element and passing them through slits. The rays also pass through an electric field and a magnetic field, and then impinge upon a photographic plate. A focussed spectrum is obtained in which the lines depend solely on the ratio of mass to charge. By varying the strengths of the two fields, any desired line may be brought on to the centre of the plate. All the measurements of the positions of the various lines are relative, and so one element must be taken as standard, and for this purpose oxygen was selected. The molecule of oxygen carries one charge, whilst the atoms carry one or two charges, with the result that with this gas three lines are obtained. The three lines are obtained at the scale readings 32, 16, and 8 respectively. Direct comparison

[4] F. W. Aston, *Phil. Mag.*, 1920, [vi], **39**, 611; *A.*, ii, **344**.

of the carbon, carbon monoxide, and carbon dioxide lines with these standards gave C++ (6), C (12), CO (28), and CO_2 (44). Clearly, therefore, the whole number relation and the additive law hold within the limit of accuracy, which is one part in a thousand.

The following results have been obtained with eleven elements. Neon, with an atomic weight of 20·2, gives two well-defined lines which correspond with masses 20 and 22 respectively. This gas, therefore, consists of two isotopes, with possibly a third, of mass 21, since there was observed a very faint line in this position.

Chlorine shows four very definite lines, corresponding with masses 35, 36, 37, and 38, with no indication whatever of a line corresponding with its atomic weight of 35·46. There is no escape, therefore, from the conclusion that chlorine is a mixture of isotopes, and that two of these have masses 35 and 37. Whilst the lines 36 and 38 may be due to two more isotopes, it is more probable that they are given by the hydrogen compounds of the two isotopes with masses 35 and 37. Strong lines were also observed at 63 and 65, due, no doubt, to the carbonyl compounds of the two isotopes. Again, if ordinary chlorine of average atomic mass 35·46 is a mixture of two isotopes 35 and 37, it is evident that the line of 35 should be stronger than the line of 37, and this was actually found to be the case. A faint line was distinguishable at 39, which possibly is due to a third isotope.

Argon shows three strong lines at 40, 20, and 13·33, which clearly correspond with particles of mass 40, carrying 1, 2, and 3 charges respectively. A faint companion was seen at 36, which is doubtless due to an isotope present in small amounts. The presence of about 3 per cent. would account for the fractional atomic weight determined from the density.

Nitrogen gives a line which cannot be distinguished from that of carbon monoxide, and a second line at 7, due to a doubly charged particle. Evidently, therefore, no isotope is present and nitrogen is a pure element.

The measurements with hydrogen were more troublesome, owing to the fact that the position of the lines is so far removed from the reference standards. The difficulty was surmounted by comparing helium with the doubly charged atoms of oxygen and carbon (8 and 6), Thomson's H_3 with carbon and helium, and hydrogen with helium. The results show definitely that both hydrogen and helium are pure elements, and that the mass of the helium atom is 4. The mean value for the mass of H_3 is 3·026, and that for the mass of the hydrogen molecule is 2·015. The atomic mass of hydrogen, therefore, is clearly 1·008, and the nature of the H_3 molecule is settled beyond question.

Krypton was found to exhibit perfectly definite evidence of being a mixture of five isotopes of masses 80, 82, 83, 83, and 86, with a probable sixth of mass 78. Measurements of these lines were made with singly, doubly, and trebly charged particles. There would seem, also, to be five isotopes present in xenon, with masses 128, 130, 131, 133, and 135, but as only a minute quantity of this gas was available these results are only provisional.

Mercury was also found to be complex, for the lines observed indicate the presence of a strong component 202, and a weak one 204. There is also a strong band from 197 to 200, indicating three or four more components, but up to the present this band has not been resolved.

Perhaps the most important generalisation that can be made from this work is the quite remarkable fact that with the exception of H_2 and H_3 all masses, atomic and molecular, elementary and compound, so far measured are whole numbers within the accuracy of experiment. The number and variety of substances studied make the probability of this being true for all elements extremely great. It certainly allows of hypotheses being put forward of atomic structure far simpler than those which attempted to explain fractional atomic weights, since these now appear to be merely fortuitous statistical effects, due to the relative quantities of the isotopic constituents. Thus it may now be supposed that an elementary atom of mass M may be changed to one of mass $M + 1$ by the addition of a positive particle (H) and an electron. If both enter the nucleus an isotope results, for the nuclear charge is unaltered. If the positive particle alone enters the nucleus, an element of the next higher atomic number is formed. When both forms of addition give a stable configuration the new elements will be isobares.

Apart from the intrinsic value of Aston's work, its importance becomes very pronounced when considered along with theories of the nuclear structure of atoms. These lead undoubtedly to integral values of atomic weights, and Harkins explains the divergence from whole numbers by the existence of isotopes. These isotopes have now been shown by Aston to exist, and it is of interest to note that Harkins has obtained evidence of the separation of chlorine into two isotopes by diffusion experiments with hydrogen chloride.[5]

On the other hand, Rutherford[6] has published further experimental data which, to a certain extent, do not fit in with Harkins' theory. When the swiftly moving particles from radium-C pass

[5] W. D. Harkins, *Science*, 1920, **51**, 289.

[6] (Sir) Ernest Rutherford, *Proc. Roy. Soc.*, 1920, [A], **97**, 374; *A.*, ii, 541.

through nitrogen, some of the atomic nuclei of this gas are disrupted, and, as is now well known, hydrogen atoms are produced. Hydrogen atoms are not produced in oxygen under the same conditions. It is found, however, that both oxygen and nitrogen give slower moving particles of mass 3 with charge 2. The nitrogen nucleus, therefore, can be disintegrated in two ways, one by the expulsion of the hydrogen atom, and the other by the expulsion of an atom of mass 3 carrying two charges. Since these atoms of mass 3 are five to ten times as numerous as the hydrogen atoms, it appears that these two forms of disintegration are independent and not simultaneous. It would follow also that the new atom when it has gained two electrons should have physical and chemical properties very nearly identical with those of helium, but with mass 3 instead of 4. The spectra of helium and this isotope should be nearly the same, but, on account of the marked difference in the relative masses of the nuclei, the displacement of the lines should be much greater than in the case of the isotopes of heavy elements like lead. It is very improbable that this isotope is connected with nebulium.

In dealing with the nuclear constitution of the lighter elements, Rutherford naturally assumes that the new helium isotope forms an integral part of these nuclei. Thus he suggests that the carbon atom consists of four atoms of the helium isotope and that the nitrogen atom consists of four of these isotopes and two hydrogen atoms, whilst the oxygen atom is built up of four helium isotopes and one helium atom. It will be seen at once that there is an essential difference between this view and that put forward by Harkins, who considers that the carbon and oxygen atoms consist of three and four atoms, respectively, of ordinary helium.

Now there seems no doubt that the helium isotope discovered by Rutherford is a different entity from H_3, which forms an integral part of Harkins' theory, was first discovered by Thomson, now confirmed by Aston, and has recently been directly prepared by the activation of hydrogen.[7] Aston has definitely shown that H_3 carries one charge, and this fact, considered along with its formation from hydrogen, shows that it is an isotope of hydrogen. There thus exist two elements of mass 3, one an isotope of hydrogen and the other an isotope of helium. It is not possible yet to say definitely whether either alone or both together take part in atomic nuclear synthesis.

In this connexion, the writer would draw attention to the very remarkable permanent contraction suffered by hydrogen when it

[7] G. L. Wendt and R. S. Landauer, *J. Amer. Chem. Soc.*, 1920, **42**, 920; *A.*, ii, 425.

has been activated and lost its activity. This point is detailed in the section of this Report dealing with the first group of elements. Wendt and Landauer assume, of course, that H_3, on keeping, regenerates ordinary hydrogen, but is it absolutely certain that this is the case? Collie's results on the formation of helium in vacuum tubes containing hydrogen, his collateral results on the permanent diminution in the volume of hydrogen in vacuum tubes, considered in connexion with the theories of atomic nuclear structure, lead inevitably to the conclusion that H_3, on keeping, gives little H_2, but mainly helium. Although this suggestion may sound very improbable to many, it is, in reality, far more probable than an ordinary chemical explanation, since it is scarcely possible to conceive that H_3 in the presence of nitrogen would not form ammonia, but prefer to react with the glass of the reaction vessel. This suggestion has been privately communicated to Dr. Wendt.

Atomic Weights.

The Report of the International Committee recommends only one change, namely, that the atomic weight of scandium should be raised from 44·1 to 45·1. The work of Hönigschmid, on which the new value is based, was referred to in last year's Report.

Three series of determinations have been made of the atomic weight of tin. Two of these involved the analysis of tin tetrabromide by silver,[8, 9] and the third depended on the direct electrolytic estimation of tin in the tetrabromide.[10] The values obtained were 118·700, 118·699, and 118·703, respectively, which agree very well with the accepted value.

The weight of a normal litre of methyl fluoride has been found to be 1·54542 grams as the mean of twenty-three determinations.[11] From this, the atomic weight of fluorine is deduced as 18·996, which is very close to the accepted value of 19.

Some determinations have been made of the atomic weight of samarium by the anhydrous chloride–silver ratio.[12] As the mean of eighteen determinations, the value of 150·43 was obtained.

In addition to the above, the following investigations may be reported. A determination has been made of the atomic weight of silicon by the analysis of silicon tetrachloride.[13] The mean of

[8] B. Brauner and H. Krepelka, J. Amer. Chem. Soc., 1920, 42, 917; A., ii, 437.　　　　　[9] H. Krepelka, ibid., 925; A., ii, 437.

[10] G. P. Baxter and H. W. Starkweather, ibid., 905; A., ii, 436.

[11] E. Moles and T. Batuecas, J. Chim. phys., 1919, 17, 537; A., i, 283.

[12] A. W. Owens, C. W. Balke, and H. C. Kremers, J. Amer. Chem. Soc., 1920, 42, 515; A., ii, 316.

[13] G. P. Baxter, P. F. Weatherill, and E. O. Holmes, jun., ibid., 1194; A., ii, 487.

four experiments gave the value of 28·11, but as this is not accepted as final by the authors, this value must await confirmation.

By the analysis of bismuth chloride, a new value for the atomic weight of bismuth has been obtained.[11] The ratio $BiCl_3 : 3AgCl$ gave 209·024, and the ratio $BiCl_3 : Ag$ gave 209·027. The mean value 209·026 is one unit higher than the value at present accepted.

Colloids.

A few papers have appeared on the preparation and properties of inorganic colloids, and mention may be made of the following. A convenient method for the preparation of metallic sols [15] is to strike an arc between poles of the metal under alcohol, using capacity in the circuit. With a current of 1·5 amperes and a capacity of $12·8 \times 10^{-3}$ MF, colloidal solutions have been obtained of aluminium, antimony, bismuth, cadmium, copper, gold, lead, platinum, silver, and zinc. The colloidal metal is produced much more rapidly than by the earlier Svedberg method. The stability of the sols is fairly great, and although a certain amount always separates, the bulk of the metal remains in solution. Gold and platinum are exceptional, since their sols are very unstable.

Colloidal rhodium [16] has been prepared by the addition of a slightly alkaline solution of formaldehyde to a slightly alkaline solution of the double chloride, Na_3RhCl_6, the reduction being carried out at 40°. Under these conditions, a clear, colloidal solution of rhodium is obtained. This solution absorbs hydrogen to the extent of 2510—2960 times the volume of rhodium present. Similarly, the rhodium absorbs 346 times its volume of carbon monoxide at 12—14°, and 1820 times its volume at 60°. The colloidal solution, slightly alkaline, causes a very slight combination of nitrogen and hydrogen to give ammonia, the reaction being considerably enhanced if the solution is made just acid with very dilute tartaric acid in the presence of potassium tartrate.

Mention may also be made of some work on the preparation and stability of mercury sols.[17] The most concentrated solution is obtained by passing a rapid stream of mercury vapour into cold water, but in every case the sols are not very stable. Their stability is materially increased by the use of gum arabic as a protective colloid.[18]

[14] O. Hönigschmid and L. Birckenbach, Zeitsch. Elektrochem., 1920, 26, 403; A., ii, 549.

[15] G. Börjeson and T. Svedberg, Kolloid Zeitsch., 1919, 25, 154; A., ii, 21.

[16] C. Zenghelis and B. C. Papaconstantinou, Compt. rend., 1920, 170, 1058; A., ii, 380.   [17] I. Nordlund, Kolloid Zeitsch., 1920, 26, 121; A., ii, 376.

[18] A. Gutbier and G. L. Weise, ibid., 1919, 25, 97; A., ii, 36.

The Rare Gases.

Mention must be made of McLennan's work on the production of helium on the large scale from natural gases.[19] A large number of gases from natural sources in various countries was investigated, and the Bow Island gas supplied to the town of Calgary, in Alberta, was selected. This gas consists of methane 91·6, ethane 1·9, nitrogen 6·14, and helium 0·36 per cent., together with traces of carbon dioxide and water vapour. It is not possible to give details of the experimental plant employed, which followed the lines of the Claude oxygen-producing column. By its means, in two stages of working helium, was obtained of 87—90 per cent. purity. By the use of a second plant, this was further purified to 98—99 per cent. From the experience gained with these experimental plants, specifications have been drawn up for a commercial plant to deal with the whole of the Bow Island supply of gas. Six units are proposed, each dealing with about 62,000 cubic feet per hour, the average daily supply of gas being 9,500,000 cubic feet. The yearly output of helium of 97 per cent. purity would be about 10,500,000 cubic feet, and the working cost would be considerably less than £10 per 1000 cubic feet.

Group I.

A most interesting paper has been published on the formation [20] of triatomic hydrogen by various means from ordinary hydrogen. Hydrogen at atmospheric pressure, when submitted to the action of α-rays from radium emanation or passed through a silent discharge tube, is converted into an active form, and a similar result is obtained when the electric discharge from a large induction coil or transformer is passed through a vacuum tube, through which hydrogen is passed under a pressure of 2—8 cm. In each case, a small amount of an active form of hydrogen is produced, which is at once condensed on passing the hydrogen through a spiral tube cooled in liquid air. This active modification reacts with sulphur, arsenic, phosphorus, mercury, and nitrogen, and also reduces acid and neutral solutions of potassium permanganate. The amount of hydrogen that is converted into the active form in the experiments described has not exceeded 0·02 per cent.

Very careful experiments have proved that the enhanced reactivity is not due to the presence of ions, and also the substance

[19] J. C. McLennan, *T.*, 1920, **117**, 927.

[20] G. L. Wendt and R. S. Landauer, *J. Amer. Chem. Soc.*, 1920, **42**, 930 ; *A.*, ii, 425.

differs in its chemical and physical properties from atomic hydrogen prepared by Langmuir, which was referred to in the Reports for 1912 and 1915. The polyatomic nature of the substance is indicated by the contraction in volume of the hydrogen when it is formed, and, moreover, positive ray analysis has shown the undoubted existence of H_3 molecules when the electric discharge is passed through hydrogen at low pressures. There is little doubt that the substance is indeed H_3.

It is very unstable, and disappears very rapidly after it has been formed. This was shown by the increased reactivity that is observed when the flow of hydrogen through the silent discharge tube is increased. At atmospheric pressures it is found that the reactivity disappears within about one minute.

Perhaps the most interesting phenomenon in these experiments is the permanent contraction that takes place in the hydrogen. This was noticed by Usher,[21] who carried out experiments on the synthesis of ammonia by exposing a mixture of hydrogen and nitrogen to the action of α-rays from niton mixed with the gases. In one case, a contraction of 0·24 c.c. was observed, but only 0·006 c.c. of ammonia had been formed. Collie and Patterson[22] observed a similar disappearance of 3·6 c.c. out of 4·6 c.c. of hydrogen when the gas was sparked under reduced pressure with copper or aluminium electrodes. A possible explanation of this phenomenon is put forward in an earlier section of this Report, and it would, indeed, seem that this may prove to be even more interesting than the preparation of H_3, great as is the importance of this advance.

Investigation has shown that lithium behaves similarly to sodium and potassium in forming soluble silicates containing a large excess of the acid over the base.[23] Lithium metasilicate, Li_2SiO_3, has been prepared in an insoluble and a soluble modification, the former having the formula Li_2SiO_3,H_2O.

Brief reference may be made to some experiments on the action of alcohol on the sulphates of sodium.[24] Dry alcohol acts on dry sodium hydrogen sulphate to give the intermediate sulphate, $Na_2SO_4,NaHSO_4$, and free sulphuric acid, which dissolves in the alcohol. No action takes place with potassium hydrogen sulphate. In the presence of moisture, sodium hydrogen sulphate is first converted into the intermediate sulphate, and then, finally, into

[21] F. L. Usher, *T.*, 1910, **97**, 389.

[22] J. N. Collie and H. S. Patterson, *P.*, 1913,' **29**, 22, 217.

[23] K. A. Vesterberg, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 30 ; *A.*, ii, 112.

[24] G. S. Butler and H. B. Dunnicliff, *T.*, 1920, **117**, 649.

ordinary sodium sulphate. When an alcoholic solution of sulphuric acid (20 per cent. or less) acts on sodium sulphate in the cold, the intermediate sulphate is formed. Nitre cake consists of $Na_2SO_4,NaHSO_4$ alone or mixed with either $NaHSO_4$ or Na_2SO_4, according as the acidity is equal to, greater than, or less than, 18 per cent. H_2SO_4.

A process has been patented for the preparation of metallic potassium by heating potassium hydroxide and sodium in exactly equivalent proportions at 670° in the absence of air.[25] Hydrogen is produced and the potassium is volatilised and may be condensed.

Some further and, it may be said, conclusive work has been carried out on the possible existence of an alkali metal of higher atomic weight than cæsium.[26] The alkalis were separated from 3500 grams of pollucite, which contains more than 30 per cent. of cæsium oxide, and the mixture was carefully tested for the presence of the next higher homologue to cæsium. There is no need to describe the experimental details, but no indication whatever was found of the presence of a new element.

Group II.

A study has been made of the equilibrium conditions which obtain between arsenic oxide, calcium oxide, and water at 35° for those mixtures in which the arsenic oxide is in excess.[27] Evidence was found of the existence of two orthoarsenates of calcium, namely, dicalcium orthoarsenate monohydrate, $CaHAsO_4,H_2O$, and monocalcium orthoarsenate, $CaH_4(AsO_4)_2$. The former is identical with the mineral haidingerite, and is stable in contact with a solution containing more than 27·5 per cent. of arsenic oxide, whilst the latter is stable with a lower percentage of arsenic oxide in the solution.

Mention may be made of the fact that chlorine has no action on calcium carbide, whilst liquid bromine slowly reacts to give hexabromoethane and calcium bromide.[28] The reaction is very slow, and 4·5 grams of the finely-powdered carbide treated with 45 grams of dry bromine for five weeks gave 22 grams of hexabromoethane, 8·8 grams of calcium bromide, and 0·2 gram of unchanged carbide.

Reference was made in the Report for last year to the fact that the decomposition of barium peroxide takes place at a much lower temperature in the presence of silica, a certain amount of barium

[25] F. C. Wickel and W. Loebel, *D.R.-P.* 307175 ; *A.,* ii, 32.

[26] L. M. Dennis and R. W. G. Wyckoff, *J. Amer. Chem. Soc.,* 1920, **42**, 985 *A.,* ii, 431.   [27] C. N. Smith, *ibid.,* 259 ; *A.,* ii, 375.

[28] E. Barnes, *Chem. News,* 1919, **119**, 260 ; *A.,* ii, 33.

silicate being formed. The influence of a great number of other oxides has now been studied by examining the heating curves of the mixtures in molecular proportions.[29] Cuprous oxide reacts violently with barium peroxide to give cupric oxide, which decomposes barium peroxide catalytically, the optimum temperature being about 660°. Magnesium and calcium oxides start the decomposition of the peroxide at 250° and 310° respectively, whilst zinc oxide causes slow decomposition between 200° and 370° and forms barium zincate. Zirconium oxide, stannous oxide, and stannic oxide have no action, but the oxides of cadmium, lanthanum, and cerium act as pure catalysts. Aluminium oxide forms barium aluminate, and titanium oxide in molecular proportions gives a titanate, probably $BaTiO_3$. With twice the molecular proportions of barium peroxide a basic titanate is produced. Litharge and barium peroxide between 300° and 400° evolve no oxygen, but form a brown substance of unknown composition. Above 500° much oxygen is evolved, with the probable formation of Ba_2PbO_4. Vanadium pentoxide reacts vigorously with barium peroxide. When equimolecular proportions are used, the reaction begins at 215° and is ended at 530°, $Ba(VO_3)_2$ being formed. With $2BaO_2$ the metavanadate is first formed, but at 375° a second, very vigorous, reaction starts and the colour changes from brown to white, the product apparently being $Ba_2V_2O_7$. Tantalum pentoxide also reacts vigorously to give a tantalate. With arsenious oxide and three molecules of barium peroxide, arsenic oxide is first formed at 310° to 410°, and above 465° oxygen is evolved and barium arsenate is formed. With antimony oxide at 200° oxygen is evolved with almost explosive violence. Bismuth oxide starts a gradual evolution of oxygen at about 250°, and higher bismuth oxides, or compounds of these with barium peroxide, appear to be formed. With chromium oxide no oxygen is evolved, and barium chromate is produced. The oxides of molybdenum, tungsten, and uranium all cause evolution of oxygen and form molybdates, tungstates, and uranates respectively. The lower oxides of manganese are all oxidised and give barium manganate. Ferric oxide acts catalytically, and gives barium ferrate, whilst nickel and cobalt also act catalytically and are changed into higher oxides, which do not agree in their properties with the known peroxides of these metals.

It has been found that strontium sulphide is readily hydrolysed by water to give equimolecular proportions of the hydrosulphide and the hydroxide.[30] These two compounds do not form a mixed

[29] J. A. Hedvall and N. von Zweigbergk, *Zeitsch. anorg. Chem.*, 1919, **108**, 119; *A.*, ii, 35.

[30] K. Brückner, *Zeitsch. Elektrochem.*, 1920, **26**, 25; *A.*, ii, 251.

compound, and the hydroxide may be separated by crystallisation. When strontium sulphide is extracted with hot water and the clear filtrate cooled, pure strontium hydroxide, $Sr(OH)_2$, crystallises. The case is different with barium sulphide, as the hydroxide and hydrosulphide form an additive compound, $OH \cdot Ba \cdot SH, 5H_2O$.[31] Under no conditions can pure barium hydroxide be crystallised from the solution obtained by the action of water on barium sulphide.

From a study of the equilibrium between zinc oxide, phosphoric oxide, and water at 25° and 37°, the following phosphates of zinc have been found to exist: $Zn_3(PO_4)_2, 4H_2O$, $ZnHPO_4, 3H_2O$, $Zn(H_2PO_4)_2, 2H_2O$, whilst at 37° an additional salt, $ZnHPO_4, H_2O$, is obtained.[32] Similar investigations with sodium hydroxide solutions and zinc oxide have established the existence of $Na_2O, ZnO, 4H_2O$ as a stable compound.[33]

Group III.

An investigation has been made of the equilibrium conditions between aluminium nitrate, nitric acid, and water at 25°, and it was found that three hydrates of the salt have a stable existence.[34] The first, $Al(NO_3)_3, 18H_2O$, is most stable in contact with the solution containing 73 per cent. or less acid, the second, $Al(NO_3)_3, 16H_2O$, is stable with 73—81 per cent. acid, whilst the third, $Al(NO_3)_3, 12H_2O$, is stable in the presence of more than 81 per cent. of nitric acid.

Some physical measurements have been made of the solutions obtained by dissolving aluminium in aqueous solutions of sodium hydroxide and of ammonium hydroxide.[35] Whilst the physical aspect of this work does not fall within the purview of this Report, the results have some value for inorganic chemists. It is shown that aluminium hydroxide neutralises the alkalis as a monobasic acid, and that the aluminates are salts of the acid $HAl(OH)_4$, that is, $Al(OH)_3, H_2O$. Ammonium aluminate, $NH_4Al(OH)_4$, is quite stable in solution.

Some further work may be reported on scandium fluoride and the scandifluorides.[36] The best method for the preparation of the

[31] K. Brückner, *Zeitsch. Elektrochem.*, 1920, **26**, 1; *A.*, ii, 252.

[32] N. E. Eberly, C. V. Gross, and W. S. Crowell, *J. Amer. Chem. Soc.*, 1920, **42**, 1433; *A.*, ii, 545.

[33] F. Goudriaan, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 179 *A.*, ii, 113.

[34] K. Inamura, *J. Tokyo Chem. Soc.*, 1920, **41**, 1; *A.*, ii, 625.

[35] J. Heyrovský, *T.*, 1920, **117**, 1013.

[36] J. Stěrba-Böhm, *Bull. Soc. chim.*, 1920, [iv], **27**, 185; *A.*, ii, 315.

pure fluoride is by the action of hydrofluoric acid on scandium oxide, the product being finally heated at 150—180° in order to remove the excess of hydrofluoric acid. Whilst the free scandifluoric acid does not exist, two new ammonium scandifluorides have been prepared. The salt, $(NH_4)_3ScF_6$,[37] is hydrolysed in the presence of ammonium fluoride to give in quadratic crystals the salt, $(NH_4)_2ScF_5$. In warm or cold water alone the salt, $(NH_4)ScF_4$, is always obtained as a microcrystalline powder. By the dissolution of scandium fluoride in a concentrated solution of silver fluoride a scandifluoride of silver is formed.

It is known that lead nitrate and nitrite interact in solution to give well-defined compounds containing both salts. Similarly, thallium nitrite and lead nitrate react to give basic compounds of both salts.[38] In the case of potassium nitrite and thallium nitrate no such double salts are obtained, but thallium nitrate–nitrites are formed which are stable and can be crystallised unchanged. With two molecules of potassium nitrite and one molecule of thallium nitrate the compound formed has the formula $Tl_3N_3O_8$. With different proportions other salts are obtained, in which the ratio between nitrate and nitrite is not a simple one.

Group IV.

Since last year's Report was written Sir Charles Parsons has published a complete account of his experiments on the artificial production of diamond.[39] It is shown beyond any doubt that high pressure alone is not sufficient to cause the conversion of graphite into diamond, and it is also shown that iron must be present. Experiments in which a mixture of acetylene and oxygen is highly compressed and a temperature produced in excess of that required to vaporise carbon, accompanied by a momentary pressure of 15,000 atmospheres, prove that the failure to produce diamond is not due to lack of temperature. Many of the experiments, in which it has been claimed that diamond is produced, have been repeated, and negative results were obtained unless iron played a part. Experiments under vacua from 75 mm. up to X-ray vacua have shown generally that as the pressure is reduced the yield of diamond is diminished. On the other hand, when alloys, previously boiled under atmospheric pressure, are quickly heated in a high vacuum, violent ebullition takes place, due to the large volume of gases liberated, and some of the contents of the crucible are ejected before

[37] R. J. Meyer, *Zeitsch. anorg. Chem.*, 1914, **86**, 257 ; *A.*, 1914, ii, 369.

L. Rollo and G. Belladen, *Gazzetta*, 1919, **49**, ii, 217 ; *A.*, ii, 34.

(Sir) C. A. Parsons, *Phil. Trans.*, 1919, [A], **220**, 67 ; *A.*, ii, 110.

they have time to part with their occluded gas, and diamond occurs in the spherules so ejected. There is no doubt that these gases, possibly containing a ferro-silicon carbonyl, are necessary for the production of diamond. It seems almost certain that the chief function of quick cooling in the production of diamond in an ingot or spherule is to bottle up and concentrate into local spots the gases occluded in the metal which, under slow cooling, would partly escape, whilst the remainder would become evenly distributed through the mass. The necessity of subjecting the iron to a temperature above 2000° before cooling would imply the necessity of carbides of silicon, magnesium, etc., being present to ensure the necessary chemical reactions with the gases at high pressure within the ingot. The greatest percentage of diamond was obtained when the atmosphere round the crucible consisted of 95 per cent. of carbon monoxide, 1 per cent. of hydrogen, 2 per cent. of hydrocarbons, and 2 per cent. of nitrogen. The weight of diamond was about 1/20,000 that of the iron. It seems probable that the rate of cooling might be so prolonged as to obtain much larger crystals and a larger total yield.

The presence of crystals of SiO_3, Al_2O_3, and MgO, the spinels, and pyrope, associated with diamond in rapidly cooled iron alloys, appears to have a bearing on the presence of similar crystals found in association with diamond, and to be compatible with Bonney's view that eclogite is the parent rock of the diamond in South Africa. It seems probable that both the eclogite and the diamond may have been simultaneously crystallised from an iron alloy. Since the average weight of diamond in the blue ground of South Africa is 1 in 5,400,000, there has been produced in cooled iron more than 270 times this amount.

Investigations were made during the war of the absorptive power of various vegetable charcoals and the improvement that is caused by heat treatment. These have now been published in part, and in the first paper the effect of heat treatment on the absorptive power of sugar charcoal for sulphur dioxide is described.[40] After heating the charcoal for forty-five hours the amount of sulphur dioxide absorbed per gram was increased from 97 c.c. to 288 c.c. In a second paper exactly analogous results were obtained, and a possible explanation is suggested.[41] The main experiments were carried out with birch-charcoal, but other wood charcoals were used. The absorptive powers were measured with sulphur dioxide, carbon dioxide, and also aqueous solutions of methylene blue. It was found that the absorptive power is very materially increased by

[40] R. M. Winter and H. B. Baker, *T.*, 1920, **117**, 319.
[41] J. C. Philip, S. Dunnill, and (Miss) O. Workman, *ibid.*, 362.

the heat treatment, with the result that the activity of animal charcoal can be paralleled and even surpassed by wood charcoal.

It was noticed that the heat-treatment is not the only factor in enhancing the activity, and the clue was found in the decrease in the bulk density of the charcoal during the heating process. If the heating is carried out in the absence of oxygen little or no improvement in the activity is produced, and oxygen must be present for the activation to take place. The explanation is probably that in the case of a freshly prepared sample the capillaries through the material are exceedingly small, so that they are soon blocked when absorption takes place. When the charcoal is heated in the presence of oxygen some oxidation takes place, and the capillaries become wider, so that the effective surface is enormously increased.

A convenient method has been described for the removal of carbon monoxide from its mixtures with other gases for analytical and hygienic purposes.[42] The carbon monoxide is very rapidly oxidised by chromic acid solution to which some mercuric oxide has been added.

Some further work on the derivatives of the silicon hydrides may be reported.[43] It was previously shown that dibromomonosilane reacts with water to form polymerides of protosiloxane, $O \cdot SiH_2$. The unimolecular form has now been obtained as a gas by the action of the required amount of water-vapour on dichloromonosilane in a very large flask under greatly reduced pressure. The compound has an extraordinary tendency to polymerise, in consequence of which the flask must be perfectly clean and smooth. Liquid and solid polymerides are formed immediately on condensation. The liquid ones are like benzene, and can be conveniently obtained as a solution by shaking a benzene solution of dichloromonosilane with water. They correspond approximately with the formula $(SiH_2O)_6$. The solid polymerides are insoluble. All the polymerides react with sodium hydroxide in accordance with the equation $SiH_2O + 2NaOH = Na_2SiO_3 + 2H_2$.

The behaviour of disilane, Si_2H_6, towards halogen acids has been investigated, and is found closely to resemble that of monosilane. Disilane does not appear to react yith hydrogen chloride at the ordinary temperature or at 120°, but in the presence of a little sublimed aluminium chloride a reaction occurs more or less readily accordng to the general scheme :

$$Si_2H_6 + xHCl = Si_2H_{6-x}Clx + xH.$$
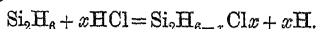
A mixture of chlorides is invariably produced, the equilibrium lying

[42] K. Hofmann, *D.R.-P.* 307614 ; *A.*, ii, 309.
[43] A. Stock and K. Somieski, *Ber.*, 1919, **52**, [B], 1851 ; 1920, **53**, [B], 759 ; *A.*, ii, 31, 429.

in favour of the intermediate members of the series. Thus with hydrogen chloride (1 vol.) and disilane (less than 1 vol.) the main product is dichlorodisilane, very little monochlorodisilane being obtained. With the gases in the volume ratio 2 : 1 much trichlorodisilane, in addition to dichlorodisilane, is obtained. Complete chlorination is not effected by a large excess of hydrogen chloride. It was not found possible to isolate monochlorodisilane in a pure state, and also the final purification of dichlorodisilane could not be effected, since it forms a mixture of constant boiling point with trichlorodisilane. There is no doubt that as in the case of the carbon compounds mixtures of isomerides are formed in the halogenation of disilane.

The bromination of disilane has been carried out in a precisely analogous manner, and monobromodisilane, m. p. $-100°$ to $-101°$, has been isolated in a state of purity.

The hydrolysis of the halogenated disilanes corresponds exactly with that of the similar monosilanes. Thus monobromodisilane reacts with water to yield the substance $(Si_2H_5)_2O$, a colourless liquid which can be volatilised without decomposition, and, when dissolved in benzene, instantaneously reduces cold silver nitrate, but not copper sulphate, solution. It reacts slowly, but quantitatively, with sodium hydroxide solution in accordance with the equation $(Si_2H_5)_2O + 8NaOH + 3H_2O = 4Na_2SiO_3 + 12H_2$. The solid products obtained by the hydrolysis of dibromodisilane and the more highly halogenated derivatives closely resemble silico-oxalic acid, $(HO_2Si·SiO_2H)x$. They are only slowly hydrolysed further by water, can be dried in a desiccator without marked decomposition, evolve hydrogen when treated with alkali hydroxide, and finally yield a residue of silicate. Evidently the Si–Si linking remains intact in them, and appears to be more stable towards alkali than was at first thought.

Amorphous zirconium may be obtained from potassium zirconium fluoride by means of sodium or aluminium, and the coherent form can be prepared from the same salt by aluminothermic reduction.[44] The coherent metal is much less chemically active than the amorphous variety, and, unlike the latter, is insoluble in all acids except hydrofluoric acid and aqua regia.

It has been shown that zirconium monoxide does not exist, the black powders obtained by the reduction of the dioxide by magnesium being mixtures of the metal and the dioxide.[45]

The iodates, perchlorates, and a chlorate have been prepared of

[44] J. W. Marden and M. N. Rich, *J. Ind. Eng. Chem.*, 1920, **12**, 651 *A.*, ii, 547.

[45] R. Schwarz and H. Deisler, *Ber.*, 1919, **52**, [B], 1896 ; *A.*, ii, 42.

zirconium.[46] The following are described: $ZrO(OH)_2,2ZrO(IO_3)_2$, $5ZrO(OH)_2,8ZrO(IO_3)_2$, $3ZrO(OH)_2,4ZrO(IO_3)_2$, $2ZrO(OH)_2,ZrO(IO_3)_2$, $3ZrO(OH)_2,ZrO(IO_3)_2$, $ZrO(ClO_4)_2,HClO_4$, $ZrO(OH)_2,9ZrO(ClO_4)_2$, and $ZrO(OH)_2,3ZrO(ClO_3)_2$.

Following the method described in last year's Report for the preparation of bismuth hydride, tin hydride has also been pre-pared.[47] It is a gas that can be condensed by liquid air and volatilised without decomposition. Some preliminary experiments seem to show that lead hydride also can exist in the gaseous state.

Group V.

Investigations have been made of the electrolysis of a solution of ammonium azide in liquid ammonia at $-67°$ with anodes of various metals.[48] The evolved gases were measured, and the loss of weight of the anode determined. Proof was obtained of the formation of the following azides: CuN_3, CuN_6, AgN_3, CdN_6, PbN_6, and SbN_9. A deep red solution of ferric azide, FeN_9, was obtained, but the compound was ammonolysed, and yielded an ammono-basic ferric azide.

The equilibrium between nitric oxide and bromine and their reaction products has been studied between $-15°$ and $330°$. With bromine at pressures below 50 mm. and at temperatures above $140°$, nitrosyl bromide is formed, the amount of the tribromide present being negligible.[49] Independent evidence of the existence of nitrosyl bromide and nitrosyl tribromide was obtained from the fusion-point diagram. The tribromide, $NOBr_3$, is a brownish-black, almost opaque, liquid, which boils with partial decomposition at $32°$.

It has been found that red phosphorus acts as a reducing agent towards many metallic salts in aqueous solution, and very possibly the method may prove of use in qualitative analysis.[50] The solution of the salt is boiled with 0·2 gram of red phosphorus for a few minutes. Mercuric and mercurous salts are reduced to the metal, gold and silver salts give insoluble phosphides, whilst palladium and osmium salts yield either the metal or a phosphide. Stannic salts are partly reduced to stannous salts, ferric salts are

[46] F. P. Venable and I. W. Smithey, *J. Amer. Chem. Soc.*, 1919, **41**, 1722; *A.*, ii, 43.

[47] F. Paneth and K. Fürth, *Ber.*, 1919, **52**, [B], 2020; *A.*, ii, 41.

[48] A. W. Browne, M. E. Holmes, and J. S. King, *J. Amer. Chem. Soc.*, 1919, **41**, 1769; *A.*, ii, 31.

[49] M. Trautz and V. P. Dalal, *Zeitsch. anorg. Chem.*, 1920, **110**, 1; *A.*, ii, 308.

[50] L. Rosenstein, *J. Amer. Chem. Soc.*, 1920, **42**, 883; *A.*, ii, 428.

reduced to ferrous, iridic salts to iridous, selenates to the element or a phosphide, molybdates to quadrivalent molybdenum salts, vanadates to tervalent vanadium salts, dichromates to chromic salts, and permanganates to manganous salts. Bismuth, lead, cadmium, antimony, and arsenic salts, arsenates, and stannous salts are not reduced, whilst tellurates and platinichlorides are very slowly reduced.

When a few drops of phosphorus trichloride are added to an aqueous solution of arsenious oxide, the solution turns yellow, then opaque-brown, and finally a copious precipitate of arsenic is thrown down.[51] The reaction probably takes place in accordance with the equation $As_2O_3 + 3PCl_3 + 9H_2O = 2As + 3H_3PO_4 + 9HCl$. The arsenic is amorphous, insoluble in carbon disulphide, and is apparently a new allotropic modification. The reaction takes place with arsenates and arsenites, and is very delicate, since the presence of 0·000075 gram of arsenic per c.c. can be detected.

Arsenic trichloride can very conveniently be prepared by passing carbonyl chloride over a mixture of arsenious oxide (80 per cent.) and carbon (20 per cent.) heated at 200° to 260°. The yield is almost quantitative.[52]

Golden antimony sulphide is usually supposed to be a mixture of Sb_2S_5, Sb_2S_3, and some free sulphur. The compound, Sb_2S_5, however, is now shown not to exist, and the golden sulphide, after extraction of the free sulphur, has the formula Sb_2S_4. This sulphide can also be prepared in the following way.[53] By the interaction of Schlippe's salt and zinc chloride, zinc thioantimonate is precipitated. The crude salt contains free sulphur, and, after removal of this, the product has the formula $Zn_3Sb_2S_8$. On treatment with dilute acid, an orange-red residue is obtained, which has the composition Sb_2S_4.

By the oxidation of bismuth oxide or hydroxide in the presence of alkali by chlorine, ammonium persulphate, or potassium ferricyanide, the higher oxides of bismuth have been prepared.[54] The tetroxide was obtained as Bi_2O_4 and Bi_2O_4,H_2O, and of each of these there are two modifications, which are brown and purplish-black respectively. A third variety, $Bi_2O_4,2H_2O$, which is yellow, has also been prepared. Bismuth pentoxide monohydrate, Bi_2O_5,H_2O, is obtained by the oxidation process, but is mixed with the tetroxide. It can be prepared from sodium bismuthate by

[51] N. N. Sen, *J. Proc. Asiatic Soc. Bengal*, 1919, **15**, 263 ; *A.*, ii, 308.

[52] L. H. Milligan, W. A. Baude, and H. G. Boyd, *J. Ind. Eng. Chem.*, 1920, **12**, 221 ; *A.*, ii, 372.

[53] F. Kirchhof, *Zeitsch. anorg. Chem.*, 1920, **112**, 67 ; *A.*, ii, 693.

[54] R. R. Le G. Worsley and P. W. Robertson, *T.*, 1920, **117**, 63.

repeated grinding with glacial acetic acid. The anhydrous oxide does not seem to be capable of existence, as the monohydrate loses both water and oxygen in a vacuum over phosphoric oxide. Bismuth hexoxide has also been prepared by the oxidation process, and is anhydrous.

Group VI.

The solubility has been determined of sulphur dioxide in sulphuric acid of various concentrations.[55] The measurements were carried out at 20°, and the acid concentration was varied from 55 to 100 per cent. It was found that a sharp minimum solubility occurs with an acid containing 86 per cent. of H_2SO_4, and it is significant that the monohydrate, H_2SO_4,H_2O, contains 84·5 per cent. of H_2SO_4.

The oxidation of ferrous chloride in presence of hydrochloric acid, and of ferrous phosphate in the presence of phosphoric acid, by sulphur dioxide has been studied.[56] In the first case, the reaction takes place in accordance with the equation

$$4FeCl_2 + SO_2 + 4HCl = 4FeCl_3 + 2H_2O + S.$$
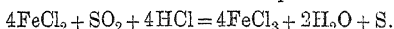
The maximum amount of ferric iron produced was about 9 per cent., and there seems little doubt that the reaction is reversible. In the second case, more ferrous salt is oxidised, and the view is expressed that the reaction

$$4Fe(H_2PO_4)_2 + 4H_3PO_4 + SO_2 = 4Fe(H_2PO_4)_3 + 2H_2O + S$$
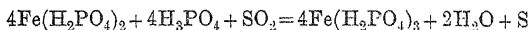
is also reversible, but that it is modified by the formation of the stable complex formed by ferric phosphate and phosphoric acid.

Group VII.

A simple and rapid method has been described for the preparation of iodine pentoxide, which depends on the oxidation of iodine to iodic acid by means of 24—26 per cent. chloric acid solution, the evaporation of the solution, and the dehydration of the iodic acid.[57] The solution of chloric acid is prepared as follows: 625 grams of barium chlorate [90 per cent. $Ba(ClO_3)_2$] are dissolved in 1 litre of nearly boiling water, and the solution is poured into an earthenware crock. The required amount of hot sulphuric acid (obtained by mixing equal volumes of concentrated sulphuric acid and water) was slowly added. It is very necessary to have a slight

[55] F. D. Miles and J. Fenton, *T.*, 1920, **117**, 59.

[56] W. Wardlaw and F. H. Clews, *ibid.*, 1093 ; W. Wardlaw, S. R. Carter, and F. H. Clews, *ibid.*, 1241.

[57] A. B. Lamb, W. C. Bray, and W. J. Geldard, *J. Amer. Chem. Soc.*, 1920, **42**, 1636 ; *A.*, ii, 615.

excess of barium chlorate rather than sulphuric acid, as the latter renders the iodine pentoxide less stable. The solution of chloric acid may be kept unchanged in glass bottles for several weeks. It is found that in the presence of 3 per cent. excess of chloric acid the net reaction with iodine is expressed by the equation

$$I_2 + 2HClO_3 = 2HIO_3 + Cl_2.$$
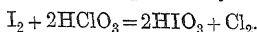
The mechanism of the reaction, however, does not consist of the direct replacement of chlorine by iodine. A considerable quantity of chloric acid is reduced to hydrochloric acid in accordance with the equation $3I_2 + 5HClO_3 + 3H_2O = 6HIO_3 + 5HCl$. A solution containing hydrochloric and iodic acids loses iodine on evaporation according to the equation $2HIO_3 + 10HCl = I_2 + 5Cl_2 + 6H_2O$. This is prevented by an excess of chloric acid, which reacts with the hydrochloric acid, and it was found that an excess of 3 per cent. is sufficient.

The iodine is oxidised in quantities of 500 grams, the reaction being finished in about twenty minutes. The iodic acid obtained on evaporation is heated at 150—160° for three hours. The final dehydration is carried out at 235—240° in a slow current of dry air. The iodine pentoxide is pure white, and has practically the theoretical oxidising value, and the yield is almost quantitative. The process has many advantages over the nitric acid method.

With reference to this preparation of iodic acid, it is interesting to note that iodine replaces bromine when the former acts on an aqueous solution of potassium bromate, and that a similar reaction does not occur with bromine and potassium chlorate, whilst the reaction between iodine and potassium chlorate is more complex.[58] The following changes have been shown to occur :

$$2KClO_3 + 2I + H_2O = KHI_2O_6 + KCl + HClO$$
and $KHI_2O_6 + KCl + HClO = 2KIO_3 + H_2O + Cl_2.$
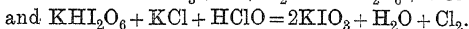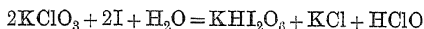
Potassium manganifluoride, K_2MnF_5,H_2O, has been prepared by the action of nitrous acid on potassium permanganate in the presence of hydrofluoric acid.[59] The permanganate is reduced by the nitrous acid. A manganous salt may also be used, in which case the nitrous acid acts as an oxidising agent.

Group VIII.

It has been found that the yield of sodium ferrate obtained by the electrolysis of sodium hydroxide solution with iron anodes is very materially increased by superposing an alternating current

[58] G. Gruber, Zeitsch. physikal. Chem. Unterr., 1920, 33, 107 ; A., ii, 684.
[59] I. Bellucci, Gazzetta, 1919, 49, ii, 180 ; A., ii, 40.

on the direct current.[60]   In one case the increase of yield was 160 per cent.   If the anode and cathode are separated, and the temperature of the electrolyte is not allowed to exceed 50°, at which the ferrates decompose, and an alternating current is super-imposed on the direct current, saturated solutions of sodium ferrate and the crystalline salt can be obtained.

Some further work has been carried out on the influence of hydrogen sulphide on the occlusion of hydrogen by palladium.[61] The earlier experiments were discussed at some length in the Report for last year.   In the earlier paper it was shown that when palladium is poisoned by hydrogen sulphide, and then heated at 100° in a vacuum, an amount of hydrogen is evolved equal in volume to that of the hydrogen sulphide previously absorbed in the poisoning.   The sulphur is retained by the palladium, a com-plex of the formula Pd_4S being formed.   Dr. Maxted believes that palladium can dissociate hydrogen sulphide to form this complex and free hydrogen slowly at ordinary temperatures.   When this takes place, more hydrogen is slowly occluded, and the total volume so occluded added to the volume derived from the hydrogen sulphide is equal to the true occlusive power of palladium for hydrogen, allowing for the palladium which has formed the Pd_4S complex.   This explanation is based on the observation that a sample of palladium which has been completely poisoned by hydrogen sulphide slowly gains a power of absorbing hydrogen up to a fixed amount, and that the rate of absorption is faster the longer the poisoned palladium is kept before the hydrogen is admitted.

This interpretation may be criticised from two points of view. In the first place, since the palladium dissociates hydrogen sulphide, it is probable that this dissociation occurs at the time of occlusion, and that it is, indeed, the basis of the occlusion.   In the second place, if palladium is absolutely completely poisoned by hydrogen sulphide, it should not gain, on keeping for an unlimited time, any power of occluding hydrogen.   Dr. Maxted offers no explanation of his view that the occlusive power for hydrogen should be increased when the hydrogen sulphide is dissociated.   True poison-ing must mean the absorption of hydrogen sulphide up to the point when a portion of the palladium is converted into the com-plex Pd_4S, and the remainder is saturated with the hydrogen obtained by the dissociation of the hydrogen sulphide.   Obviously, when this has been secured, no further hydrogen can be occluded. It would seem far more probable that the poisoning obtained with

[60] G. Grube and H. Gmelin, *Zeitsch. Elektrochem.*, 1920, **26**, 153 ; *A.* ii, 377.   [61] E. B. Maxted, *T.*, 1920, **117**, 1280.

hydrogen sulphide is not complete in the strict sense, but that the poisoning is concentrated on the surface. On allowing the partly poisoned palladium to remain, a more equal distribution of the hydrogen takes place, with the result that more hydrogen can be occluded. This is shown by the fact that, even after the palladium has been "completely" poisoned by hydrogen sulphide, it still possesses the power of slowly absorbing more hydrogen sulphide.

The data are still too incomplete for accurate calculations of the true equilibrium conditions. It appears that 1 gram of palladium has the definite power of absorbing 69 c.c. of hydrogen. Is the whole of this hydrogen dissociated into atoms, or are there two processes, first the occlusion of hydrogen as atoms, followed by a secondary effect of condensation as hydrogen molecules? The second alternative seems the more probable, but the question can only be decided by accurate measurements of the dissociation pressures of hydrogenised palladium.

An investigation has been made of the hydrolysis of aqueous solutions of potassium platinichloride.[62] It is shown that $N/50$ and more concentrated solutions are slowly and completely hydrolysed in the dark, whilst $N/100$ and more dilute solutions undergo hydrolysis only when exposed to light. It is found that the hydrolysis takes place at first very slowly, but after a time the rate increases, and this is attributed to the formation of some substance which acts as a catalyst. This view was supported by the fact that the addition of a portion of a photochemically hydrolysed solution to a fresh $N/100$-solution of platinichloride causes the latter to undergo hydrolysis in the dark.

The addition of a soluble chloride to the hydrolysed solution causes a complete reversal of the reaction, and this reverse reaction is influenced by light in much the same way as is the direct reaction. The influence of platinum-black in accelerating both the direct and reverse reactions in the dark is quite noticeable, but is not measurable when light is acting on the solutions.

<div align="right">E. C. C. BALY.</div>

[62] E. H. Archibald, *T.*, 1920, **117**, 1104.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

A SURVEY of the literature shows that few laboratories have yet been able to devote much of their energies to systematic research on the pre-war scale. The present Report deals only with such papers as the writer considers of importance from the theoretical point of view or for new methods of preparation. A distinctive feature of this year's literature is the number of papers dealing with the compounds used so extensively in chemical warfare, and with alternative methods for the synthesis of substances of which there was a scarcity in the belligerent countries.

Hydrocarbons.

Very few investigations on hydrocarbons have been described during the year, but it is of interest to gauge the success attending the strenuous efforts made in Mid-Europe to use paraffin for the production of fatty acids and their esters to overcome the shortage of natural fats. The usual method was to heat the hydrocarbons of high molecular weight with oxygen or air, generally under pressure in the presence of a catalyst. Thus, in the presence of manganese compounds, C. Kelber[1] converted a paraffin wax (m. p. 50°), by the action at 150° of a stream of finely divided oxygen, into a mass of which more than 35 per cent. consisted of fatty acids insoluble in water, and about 25 per cent. of the lower (up to C_{10}) fatty acids.

H. H. Franck[2] used also up to 5 per cent. of various compounds of lead, mercury, vanadium, and chromium, and, working at 150° in an autoclave filled with oxygen, obtained from paraffin of lower melting point 40 per cent. of fatty acids of higher, and 57 per cent. of acids of lower, molecular weight. A mixture of the acids so obtained was esterified with ethylene glycol, and yielded an edible fat said to resemble coconut oil. A variation is described

[1] Ber., 1920, 53, [B], 66, 1567 ; A., i, 280.
[2] Chem. Zeit., 1920, 44, 309 ; A., i, 417.

by F. Fischer and W. Schneider,[3] who worked in a steel autoclave at 170° in the presence of sodium carbonate, the mixture being stirred by pumping in compressed air. These authors obtained a 90 per cent. yield of fatty acids from crude paraffin, and are of the opinion that iron, copper, and manganese have equal catalytic effects. A. Grün[4] has studied these reactions more in detail, and shown that the results are dependent on many factors as yet little understood. In the absence of water the anhydrides of the higher fatty acids are formed, and in every case the neutral products contain ketones, such as stearone. The acids formed all appear to have a "straight-chain" structure, whilst, according to Fischer and Schneider, the acids containing an uneven number of carbon atoms are formed in greater quantity than those with an even number, which are commonly derived from natural fats.

The list of compounds formed in the pyrogenic condensation of acetylene has been considerably increased[5] by the crystallisation of the picrates of the higher boiling fractions of the tar. It has been shown[6] that acetylene condenses at 100—200° with methane in the presence of metallic catalysts, giving a 70 per cent. yield of propylene; at higher temperatures (200—350°), non-metallic catalysts, such as thoria and silica, give similar results[7] even with at least the lower homologues of both acetylene and methane.

The importance of a study of the mercury compounds of acetylene was emphasised in last year's Report, and attention should be drawn to the theoretical discussion by W. Manchot and A. Klüg[8] of those of ethylene and of carbon monoxide. A detailed study of the conversion of acetylene into acetaldehyde and into acetic acid in the presence of mercury catalysts is described by B. Neumann and H. Schneider.[9] The best yield (90 per cent.) of acetaldehyde was obtained when the gas was led with vigorous mechanical stirring into a catalyst composed of 96 per cent. acetic acid, containing 3 per cent. of mercuric sulphate, the temperature being maintained at about 30°. The best results (83 per cent. yield) in the direct conversion of acetylene into acetic acid were obtained by using the same catalyst, with the addition of vanadium pentoxide, acetylene and oxygen being led in alternately.

[3] *Ber.*, 1920, **53**, [B], 922; *A.*, i, 519.   [4] *Ibid.*, 987; *A.*, i, 518.

[5] R. Meyer and K. Taeger, *ibid.*, 1261; *A.*, i, 589.

[6] A. Heinemann, *D.R.-P.* 315747; *A.*, i, 281.

[7] Chemische Fabrik Buckau, *D.R.-P.* 294794; *A.*, i, 657.

[8] *Annalen,* 1920, **420**, 170; *A.*, i, 720; also *Ber.*, 1920, **53**, [B], 984; *A.*, i, 519.

[9] *Zeitsch. angew. Chem.*, 1920, **33**, 189; *A.*, i, 657.

Alcohols and their Derivatives.

In the catalytic reduction of acetaldehyde by hydrogen, the production of ethyl alcohol falls off gradually with the formation of ethyl ether as a by-product, whilst the catalyst is poisoned by decomposition products of acetaldehyde. These undesirable results are avoided [10] by the use of an excess of hydrogen containing about 0·2 per cent. of oxygen, and when working between 90° and 170°, at which temperature acetaldehyde begins to decompose, a yield of 95 per cent. of alcohol can be obtained. The beneficial effect of the oxygen cannot, however, be wholly attributed to the oxidation of carbon monoxide or other impurities, to the presence of which the injurious effect on the catalyst has been ascribed. If hydrogen quite free from oxygen be used (and it is stated that electrolytic hydrogen invariably contains some oxygen), a mixture of alcohol and ether is produced. The formation of ether commences at about 90°, and in the process up to 15 per cent. is obtained.

The formation of acetone by the fermentation of starch is dependent as a commercial process on the utilisation of the *n*-butyl alcohol, of which at least two parts are produced for every one of acetone.[11] In this connexion the transformation of the alcohol into methyl ethyl ketone is promising,[12] as the various reactions proceed quite smoothly. These are: The catalytic dehydration of the alcohol by glacial phosphoric acid at about 350°, the absorption of the β-butylene (freed from γ-butylene by scrubbing with 60 per cent. sulphuric acid) in concentrated sulphuric acid, formation of *sec.*-butyl alcohol by the action of water on the butyl hydrogen sulphate thus produced, and the catalytic dehydrogenation by copper of the *sec.*-butyl alcohol by the Sabatier and Senderens process. The use of *n*-butyl alcohol as a starting material for various synthetical reactions, such as the preparations of *n*-amyl alcohol, *n*-valeric and *n*-hexoic acids, has been studied by R. Adams and C. S. Marvel.[13] The writer can recommend their methods, which give very good yields and are well adapted for students' exercises in place of some of the preparations usually set.

Further condensations of *n*-butyl alcohol with the corresponding aldehyde,[14] and of *n*-butyl chloroformate [15] with alcohols and

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[10] Elektrizitätswerk Lonza, *Brit. Pat.* 134521 ; *D.R.-P.* 317589 ; *A.*, i, 134.

[11] J. Reilly, W. J. Hickinbottom, F. R. Henley, and A. C. Thaysen, *Biochem. J.*, 1920, **14**, 229 ; *A.*, i, 465.   [12] A. T. King, *T.*, 1919, **115**, 1404.

[13] *J. Amer. Chem. Soc.*, 1920, **42**, 310 ; *A.*, i, 283.

[14] C. Weizmann and S. F. Garrard, *T.*, 1920, **117**, 324.

[15] F. D. Chattaway and E. Saerens, *ibid.*, 708.

amines, according to well-known reactions have also been described. A. Mailhe and F. de Godon [16] have continued their studies of the catalytic preparation of ethers in the dry way, and recommend aluminium oxide (prepared by heating commercial ammonium alum at 190°) as a catalyst. This method gives about 70 per cent. of diethyl ether from 96 per cent. alcohol, and is suitable for the preparation of simple and mixed aliphatic ethers containing normal groups, but fails with *iso*propyl and *iso*butyl alcohols, and gives only a 30 per cent. of the corresponding ether from allyl alcohol.

The catalytic effect of mineral acids in esterification is attributed to their linking the alcohol and organic acid in a molecular complex, where opportunity is afforded for an interchange of radicles. While investigating this, O. Maass and J. Russell [17] have proved the existence of an oxonium compound, $(C_2H_5)_2O,HBr,H_2O$, but could not obtain definite evidence of a compound of ether, hydrogen bromide, and ethyl alcohol. Very similar suggestions are made by O. Aschan,[18] who explains the catalytic effect of ether in aiding the addition of hydrogen chloride and of sulphuric acid to unsaturated compounds as due to the intermediate formation of diethyloxonium salts. He shows that the mixing of ether and sulphuric acid monohydrate causes a large development of heat, and gives a mixture more viscous than the sulphuric acid, but he was unable to isolate the diethyloxonium sulphate or any of its salts.

Lowry and co-workers [19] describe experiments to recover the oxidised nitrogen in cordite in the form of calcium nitrate. They consider that hydrolysis of the normal type is not the predominant action when cordite is decomposed by lime in the presence of pyridine. The calcium salt of hydroxypyruvic acid is an important product of the reaction, and these authors suggest that the main action is a decomposition of the nitric ester into a ketone or aldehyde and a nitrite. R. C. Farmer,[20] however, from a review of their work and that of the numerous previous workers at this problem, and from some fresh experimental data on the decomposition and hydrolysis of glyceryl nitrates, disagrees with their conclusions and, tracing the various stages of the different forms of decomposition of nitric esters, maintains that the first stage in such is a true ester hydrolysis of the normal type.

[16] *Bull. Soc. chim.*, 1919, [iv], **25**, 565; 1920, [iv], **27**, 121, 328; *A.*, i, 6, 284, 470.

[17] *Trans. Roy. Soc. Canada*, 1919, **13**, [iii], 259; *A.*, i; 521.

[18] *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 8; *A.*, i, 136.

[19] T. M. Lowry, K. C. Browning, and J. W. Farmery, *T.*, 1920, **117**, 552.

[20] *Ibid.*, 806.

Aldehydes and Ketones.

The oxidation of methyl alcohol to formaldehyde has been investigated by many workers in the past, but the latest contribution to the subject is valuable. In this, M. D. Thomas[21] compares the relative catalytic effect on the oxidation under different conditions of silver, gold, and copper. Of these, silver has the best effect, and by its use a yield of more than 55 per cent. was obtained in the process. Finely divided silver,[22] preferably deposited on asbestos, is recommended also for the catalytic oxidation by air at about 250° of primary and secondary alcohols to the corresponding aldehydes and ketones. The action tends to become very intense owing to rise of temperature of the catalyst, but if care be taken to regulate this, the method can be employed generally with success even with unsaturated alcohols.

A new and in some cases a very useful method of preparing aldehydes is patented by C. Harries,[23] who shows that ozonides can be reduced preferably by ferrocyanides to aldehydes, nonaldehyde, for example, being formed by the reduction of the ozonide of oleic acid.

The great diversity in the type of compounds which acetylacetone forms with metals, metalloids, and non-metals has now been extended by the discovery of a new type in the selenium and tellurium acetylacetonates, which are described in a paper[24] bearing on the complex questions of residual affinity and co-ordination.

An attempt[25] to use the additive compounds of the acetylacetonates of the metals of the rare earths with ammonia and amines as a convenient means of separating these elements was, however, quite unsuccessful.

Acids and their Derivatives.

Very little work in this section has been published during the year. The details[26] of a much improved method of preparing gluconic acid on a technical scale suggest that this may be utilised as a substitute for some of the more expensive vegetable acids.

[21] *J. Amer. Chem. Soc.*, 1920, **42**, 867 ; *A.*, i, 473.

[22] C. Moureu and G. Mignonac, *Compt. rend.*, 1920, **170**, 258 ; *A.*, i, 283.

[23] *D.R.-P.* 321567 ; *A.*, i, 675.

[24] G. T. Morgan and H. D. K. Drew, *T.*, 1920, **117**, 1456.

[25] G. Jantsch and E. Meyer, *Ber.*, 1920, **53**, [B], 1577 ; *A.*, i, 711.

[26] A. Herzfeld and G. Lenart, *Zeitsch. Ver. deut. Zuckerind.*, 1919, 122 ; *A.*, i, 143.

The well-known work of K. Meyer and co-workers on the keto-enolic desmotropy of the esters of β-ketonic acids has been extended [27] to an examination of the effect of fractional distillation on ethyl acetoacetate. By the use of Jena-glass apparatus, which had been steamed and washed with alcoholic hydrogen chloride, it has been found possible to isolate the less volatile ketonic form by distillation under a pressure of 2 mm. The proportion of enol to ketone is unaffected by distillation, for the actual amounts of the two forms in the original ester before distillation in a quartz vessel and in three fractions and a residue, all of equal volume, were practically the same, whilst the residue was free from the enolic form. The method obviously affords the easiest means of preparing the pure ketonic ester, and by repeated distillation of large amounts of the ester might yield the pure enolic form. Similar results are recorded for the distillation of methyl benzoylacetate, although the fractionation proceeds more slowly, but with this ester a small first fraction solidified to give the pure enolic form. For many years it has been the practice to postulate the existence of enolic forms of aliphatic esters to explain certain reactions. H. Scheibler and J. Voss [28] have shown that the potassio-derivatives of esters, which contain at least one hydrogen atom attached to the carbon atom in the α-position with respect to the carbalkyloxy-group, are readily obtained as coloured amorphous substances when an ethereal solution of the ester is added to the finely divided metal, which is covered with ether heated to gentle ebullition; under these conditions the metal dissolves immediately with evolution of hydrogen, whilst the metallic derivative remains more or less completely in colloidal solution in ether. Sodium acts less energetically, and the corresponding derivatives are often only formed at temperatures at which they are partly decomposed. These ester-enolates are very unstable substances, which can, however, be preserved for some time under ether in an atmosphere of hydrogen or nitrogen. They are immediately decomposed on the addition of water with the regeneration of the esters, but react with carbon dioxide, giving colourless potassium salts of carboxylic acids, which are stable towards oxygen and water, but contain the carboxylic group in a very loose state of combination. So far not much evidence has been brought forward to prove the formulæ ascribed to these compounds, but the reaction between ethyl chloroformate and ethyl potassio-acetate can be to some extent explained on the basis of the formula CH_2:$C(OK)\cdot OEt$.

Many difficulties are met with when attempts are made to syn-

[27] K. H. Meyer and V. Schoeller, *Ber.*, 1920, **53**, [B], 1410 ; *A.*, i, 707.
[28] *Ibid.*, 388 ; *A.*, i, 366.

thesise the natural fats. Up to the present the general methods for the preparation of mono- and di-glycerides have depended either on the action of glyceryl chlorohydrins on the salts of fatty acids or on esterification of the fatty acid with the chlorohydrin, and the subsequent exchange of the halogen atoms for the hydroxyl group. Now the glyceryl monochlorohydrins [29] are difficult to prepare in a state of purity, and are not adapted for such synthetical reactions, as these methods are complicated by side-reactions. There is, further, no guarantee of the simple replacement of the halogen by the acyl radicle, whilst, in fact, several instances of the wandering of such acyl groups are now known.[30] A new method, which will yield α-monoglycerides of undoubted purity, is published [31] under the names of Emil Fischer and co-workers. As initial material "acetone glycerol" is used, and the constitution of this has been shown by Irvine, Macdonald, and Soutar [32] to be

*iso*propylideneglycerol, $CMe_2\diagdown^{O \cdot CH_2}_{O \cdot CH \cdot CH_2 \cdot OH}$.   This compound

reacts readily in the presence of quinoline with acid chlorides, yielding products from which the acetone residue is easily removed by dilute acids at about 50°, thus giving undoubted α-monoglycerides. The results of this important work throw great suspicion on the purity of the monoglycerides previously described, whilst it may be expected that the method, even without the guiding hand of Fischer, will lead to further knowledge of the chemistry of fats.

Halogen Compounds.

One of the less pleasant features of the literature this year is the large amount of space which has been devoted to descriptions of various halogen compounds used so extensively in chemical warfare. The preparation and properties of $\beta\beta'$-dichlorodiethyl sulphide have been detailed in the chemical journals of five countries, in the allied countries it having been made very simply by the action [33] of sulphur monochloride on ethylene at about 60°, whilst in Germany the more complicated synthetic process through ethylene chlorohydrin and $\beta\beta'$-dihydroxydiethyl sulphide was used as described by Victor Meyer in 1886. Several chemists have used the highly reactive dichlorosulphide for various synthetical

[29] L. Smith and E. Samuelson, *Zeitsch. physikal. Chem.*, 1920, **94**, 691; *A.*, i, 658.

[30] E. Fischer, *Ber.*, 1920, **53**, [B], 1621; *A.*, i, 808.

[31] E. Fischer, M. Bergmann, and H. Bärwind, *ibid.*, 1589; *A.*, i, 805.

[32] *T.*, 1915, **107**, 337.

[33] (Sir) W. J. Pope, C. S. Gibson, and H. F. Thuillier, *Brit. Pat.* 142875; *A.*, i, 523.

experiments, of which perhaps the most complete account is that by O. B. Helfrich and E. E. Reid.[34]

French chemists[35] have made very detailed studies of the numerous compounds produced by the substitution of hydrogen by chlorine in methyl formate and carbonate; it may be expected that some of these will be of considerable use in synthetical work.

A very convenient modification of the older methods of preparing alkyl bromides is described by O. Kamm and C. S. Marvel.[36] In this a solution of hydrobromic acid is first prepared by the reduction of bromine by sulphur dioxide in the presence of water. Concentrated sulphuric acid is then added, and the mixture heated under a reflux with the alcohol to be brominated. The method can be recommended, as it gives good yields with very little trouble.

$\alpha\beta$-Dichlorovinyl ethyl ether is readily prepared from the commercial trichloroethylene by the action of sodium ethoxide, and has been found useful in the synthesis of chloroacetates and acid chlorides.[37]

Numerous new per-iodides of carbonyl compounds[38] and esters[39] have been described, and it is remarkable that those prepared from diethyl oxalate of the type $(C_2O_2Et_2)_4,NaI,I_4$ were obtained in the presence of water. These compounds are apparently oxonium derivatives, and will require consideration from those studying residual valency.

Optical Activity.

It has been well known in a few cases that the taste of some optically active compounds is different from that of their optical antipodes. This very difficult field of research has not received much attention, and an interesting paper[40] on the relative sweetness of some compounds of α-hydroxy*iso*hexoic or "leucic" acid is all the more welcome. It is a common practice in Japan to use certain amino-acids, such as d-glutamic acid and its salts, as taste-producing substances in food, and the author, by replacing the amino-group in some of these by hydroxyl, has obtained some very sweet substances. Thus, by suitable treatment, leucine has been converted into the corresponding hydroxy-acid. The sodium, ammonium, potassium, and calcium salts are very sweet, the sodium

[34] *J. Amer. Chem. Soc.*, 1920, **42**, 1208 ; *A.*, i, 524.

[35] *Inter alia*, V. Grignard, G. Rivat, and E. Urbain, *Compt. rend.*, 1919, **169**, 1143 ; *A.*, i, 138.

[36] *J. Amer. Chem. Soc.*, 1920, **42**, 299 ; *A.*, i, 282.

[37] H. Crompton and (Miss) P. L. Vanderstichele, *T.*, 1920, **117**, 564.

[38] A. M. Clover, *J. Amer. Chem Soc.*, 1920, **42**, 1248 ; *A.*, i, 528.

[39] A. Skrabal and E. Flach, *Monatsh.*, 1919, **40**, 431 ; *A.*, i, 527.

[40] S. Kodama, *J. Tokyo Chem. Soc.*, 1919, **40**, 825 ; *A.*, i, 471.

salt being about ten times as sweet as sucrose. The taste is apparently due to the α-hydroxy*iso*hexoic ion, since all the salts and the acid itself in dilute solution are sweet, whilst the solid acid and its ester are not. It is remarkable that the two anhydrides of leucic acid with the formulæ $C_4H_9 \cdot CH {<}^{CO \cdot O}_{O \cdot CO}{>} CH \cdot C_4H_9$ and $C_4H_9 \cdot CH(OH) \cdot CO \cdot O \cdot CH(CO_2H) \cdot C_4H_9$ are bitter, but become sweet when boiled with dilute alkalis. The acetyl and alkyl derivatives of the leucic acid are not sweet, and their salts are tasteless, but a salt of acetyl-leucic acid when boiled with water slowly becomes sweet, owing to the elimination of the acetyl group. The sweetness of *d*-glutamic acid is twice as great as that of the *dl*-acid, and the sweetness of a salt of leucic acid depends on the amount of the dextrorotatory form which is present. Thus, having obtained by a Walden inversion a dextrorotatory leucic acid from the corresponding *l*-acid, the author shows that the salts of the *d*-acid are sweeter than those of the *dl*-acid, which are also sweeter than those of the *l*-acid.

Some years ago Hudson suggested that the difference between the molecular rotations of the α- and β-forms of mutarotatory sugars is a constant, and afterwards extended these views [41] to the phenylhydrazides of certain acids of the sugar group. He succeeded in showing that in acids containing α-, β-, γ-, and δ-asymmetric carbon atoms, the rotation due to the α-carbon atom was very much larger than the values due to the other three carbon atoms added together, and so the direction of the rotation of the phenylhydrazide could be used as an indication of the configuration of the hydroxyl group attached to the α-atom. His results have now received valuable confirmation from the extended investigation of Mlle. T. W. J. van Marle,[42] who, working with gluconic, mannonic, galactonic, gulonic, idonic, *iso*saccharic, arabonic, ribonic, xylonic, and lyxonic acids, has been able to prove that Hudson's conclusions hold equally in aqueous solution for the hydrazides, *p*-bromophenylhydrazides, *o*-, *m*-, and *p*-tolylhydrazides, the amides, anilides, and *o*-, *m*-, and *p*-toluidides. It is not surprising, however, that conflicting results were obtained when the rotations of these compounds were examined in pyridine solution, and in the opinion of the writer it seems a great pity, in view of the results obtained in recent years in the domain of optical activity, that the material prepared with so much trouble for this research was not examined with monochromatic light of more than one wave-length.

[41] *J. Amer. Chem. Soc.*. 1917, 39, 462 ; *A.*, 1917, i, 318.
[42] *Rec. trav. chim.*, 1920, 39, 549 ; *A.*, i, 592.

The hydrolysis of the esters of certain optically active hydroxy-acids has yielded in the past very perplexing results, and a summary [43] of the behaviour on hydrolysis of the optically active menthyl and bornyl esters of the various isomeric "phenyl-lactic" and other acids. Mandelic acid and tropic acid,

$$C_6H_5 \cdot CH(CH_2 \cdot OH) \cdot CO_2H,$$
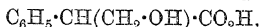
are racemised readily, and their esters are catalytically racemised by warming with an amount of alcoholic solutions of sodium or potassium hydroxide insufficient to complete the hydrolysis; on the other hand, the acids $C_6H_5 \cdot CH_2 \cdot CH(OH) \cdot CO_2H$,

$$C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO_2H,$$
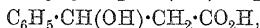
and $C_6H_5 \cdot CMe(OH) \cdot CO_2H$, and their esters, are far less prone to racemisation. Thus it appears that although compounds of the type $R \cdot CH(OH) \cdot CO_2R'$ present a system prone to racemisation in virtue of the mobile hydrogen atom being in the α-position, this circumstance is not in itself a factor in promoting racemisation unless R is an aromatic residue attached directly to the asymmetric atom. In the event of R being an aliphatic group, it may be argued that this system would probably be stable, so far as race-misation by alkali is concerned, and this is confirmed to some extent by experiments with lactic acid.

C. Neuberg and F. F. Nord [44] have investigated the phyto-chemical reduction of unsymmetrical ketones. These, added to sucrose undergoing fermentation by yeast, are partly reduced to secondary alcohols. The hydrogenation does not proceed at all readily, but the diastereoisomerides are formed at different rates, so that the products, whilst not optically pure, have a considerable activity, which is much greater than observed by Le Bel in his classical experiments on the preferential decomposition by moulds of the diastereoisomerides of secondary alcohols. They claim also to prepare a lævorotatory $\beta\gamma$-butylene glycol by the hydrogenation of diacetyl by similar means, a result which is all the more remark-able as previous investigators have found that the production of the glycol from carbohydrates by bacterial agency leads only to the racemic or *meso*-forms.

An interesting attempt [45] has been made to summarise the phenomena observed among the optically active substances found in the animal and plant kingdoms. Whilst there are several exceptions, it would appear that, in general, the normal products of animal metabolism occur in optically active forms, but in the case of the plant organism, on the other hand, the diastereo-

[43] A. McKenzie and H. Wren, *T.*, 1920, **117**, 680.

[44] *Ber.*, 1919, **52**, [B], 2237, 2238; *A.*, i, 135.

[45] K. Hess and W. Weltzien, *ibid.*, 1920, **53**, [B], 119; *A.*, i, 328.

isomerides are not infrequently formed in equal amounts. It is probable, however, that the specific action of an enzyme is only conditional, and that whilst a ferment appears to attack preferentially one modification of a given compound, it can, in case of necessity, attack the antipode, or it may be that whilst under normal conditions the rate of reaction between an enzyme and the two diastereoisomerides is different, when the conditions are suitable the rate becomes identical. The production of optically inactive bases containing an asymmetric carbon atom may be ascribed, however, to other causes. Thus, racemisation of a primarily formed optically active alkaloid may have occurred during the treatment of the dead plant with extracting solvents, or it may have occurred within the plant during its life, or, again, the formation of the alkaloid in the living plant may have been brought about by ordinary symmetrical forces in which enzymes have no part. It is well known, however, that alkaloids vary very greatly in their resistance to racemising reagents; thus hyoscyamine is readily converted by alkalis into atropine, and pelletierine and allied substances are less prone to racemisation in this way, whilst coniine and d-methylconiine are unchanged by drastic treatment with acids or alkalis.

E. Erlenmeyer [46] has described the formation of optically active cinnamic acids. It is suggested that the activation of the cinnamic acid is brought about by the "induction" influence of other optically active components involved in the reactions. Thus when an optically active phenylbromolactic acid is reduced with zinc in hot alcoholic solution, one half of it passes into phenyl-β-lactic acid and the other half into cinnamic acid, which has a rotation of the same sign as that of the bromo-acid. The activity of the resulting cinnamic acid is not due to contamination with phenyl-lactic acid, as repeated extractions with water still leave an active cinnamic acid, and this is further confirmed by comparative experiments with actual mixtures of optically inactive cinnamic acid and active phenyl-lactic acid. In a similar manner, a lævorotatory dibromide of cinnamic acid is formed by the action of bromine on a mixture of the zinc salts of cinnamic and d-phenyl-lactic acid, an opposite result being obtained when l-phenyl-lactic acid was used. The reduction products of l- and of d-phenylbromolactic acids in the same way yield dibromides of cinnamic acid with rotations opposite in sign to that of the bromo-acids employed. Further experimental results obtained are: cinnamic acid "activated" under the influence of l-mandelic or l-chlorosuccinic acid becomes dextrorotatory and yields a lævorotatory dibromide, whilst with d-tartaric

[46] Biochem. Zeitsch., 1919, 97, 198 ; A., i, 45.

acid or with d-cinchonine, a lævorotatory acid and dextrorotatory dibromide are formed.

As the geometrical isomeric formula of cinnamic acid with the double bond cannot account for the active cinnamic acids, the author suggests a stereoisomeric structure with free unsaturated affinities, thus:
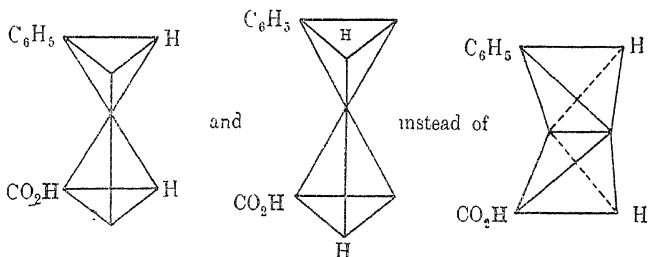
Recent work by Lowry and others has stimulated a re-examination of the menthyl esters of certain keto-acids described previously by Rupe [47] and his co-workers. The rotations of these were observed only for sodium light, but light of other wavelengths has now been used. Most of these substances are not, however, homogeneous, containing varying proportions of the enolic and ketonic forms, according to the conditions. However, the authors "re-discover" the applicability of a one-term Drude equation, $a = k/\lambda^2 - \lambda_0^2$, as has been shown by Lowry and other investigators, to the optical dispersion of a great number of compounds. They adopt the following classification of abnormal rotatory dispersion: (i) total anomaly of a mixture of two substances with opposed activities (Tschugaev's extramolecular anomalous dispersion); (ii) total anomaly of a compound containing two different asymmetric complexes, one of which is dextro-, the other lævo-rotatory (Tschugaev's intramolecular anomalous dispersion); (iii) when the rotatory dispersion curve does not pass through a maximum or minimum, neither does it approximate to a horizontal line, but λ and λ_0^2 differ widely from the normal values and $\dfrac{1}{\alpha}/\lambda^2$ gives bent or zig-zag lines (complex rotatory dispersion of Lowry); (iv) apparently normal course of the curves and $\dfrac{1}{\alpha}/\lambda^2$ gives straight lines, but λ_a and λ_0^2 differ greatly (at least $\pm15\,\mu\mu$ for the former) from the normal value for the particular class of compound (relative anomaly).

[47] H. Rupe and H. Kägi, *Annalen*, 1920, **420**, 33 ; *A.*, i, 748.

The paper contains a criticism of the proposal by Lowry and Abram [48] to delete the "relatively abnormal" classification; the authors consider that sufficient substances are known, in which λ_a differs by 15—60 $\mu\mu$ and λ_0^2 by as much as five units from the normal figures for the class of substance without, however, exhibiting complex anomaly, to justify a separate classification.

It may be pointed out, however, that many substances have rotations which are numerically low, whilst the accuracy of the determination of rotatory power is not very great, so that in the opinion of the writer it is unwise in the present state of knowledge to adopt the more elaborate classification set out by Rupe.

Carbohydrates and their Derivatives.

In 1913 Emil Fischer [49] obtained a strongly reducing compound, $C_6H_{10}O_4$, which he named glucal, by the reduction of β-acetobromoglucose with zinc dust and acetic acid. It is a slightly sweet, soluble, viscid syrup with aldehydic properties, and evidently possesses ethylenic unsaturation, since it decolorises bromine water. When hydrogenated in the presence of palladium, hydroglucal is formed, and this contains no double bond; the same product is formed if the acetate of glucal is similarly hydrogenated and then hydrolysed. The constitution of glucal has not been conclusively proved, but the latest paper [50] shows that its properties are satisfactorily explained by the formula

$$OH \cdot CH_2 \cdot CH(OH) \cdot CH \cdot CH(OH) \cdot CH \colon CH.$$
$$\underline{\qquad\qquad O \qquad}$$
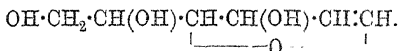
New reactions pointing to this formula are: (*a*) the additive product of glucal and bromine, when treated with silver acetate, yields a stereoisomeric mixture of tetra-acetylglucose-β-bromohydrins, $OAc \cdot CH_2 \cdot CH(OAc) \cdot CH \cdot CH(OAc) \cdot CHBr \cdot CH \cdot OAc$, which, after
$$\underline{\qquad -O \qquad\qquad}$$
deacetylation with dilute hydrochloric acid, gives with phenylhydrazine an over-all yield of 60 per cent. of *d*-glucosephenylosazone; (*b*) glucal triacetate is transformed by ozone in glacial acetic acid solution into the triacetyl derivatives of *d*-arabinose and an acid, which is probably arabonic acid; (*c*) the colour reaction with pine shavings; (*d*) the proof of the presence of only three hydroxyl groups in hydroglucal. These show that glucal contains the normal carbon chain present in dextrose, that the double bond

[48] *T.*, 1919, **115**, 300.

[49] *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 311 ; *A.*, 1913, i, 445.

[50] E. Fischer, M. Bergmann, and H. Schotte, *Ber.*, 1920, **53**, [B], 509 ; *A.*, i, 420.

is between the first and second carbon atoms, and that it is related to furan, whilst the presence of a butylene-oxide formation in hydroglucal is suggested by its stability towards hydrochloric acid, which renders an ethylene- or propylene-oxide structure most improbable.

The structural formula for sucrose which is now considered the most likely is that put forward by W. N. Haworth and Law in 1916, in which this sugar is represented as formed by the fusion of α-glucose having the butylene-oxide structure, and of α-fructose having the ethylene-oxide structure:

$$CH_2 \cdot OH$$
$$OH \cdot CH_2 \cdot CH(OH) \cdot CH \cdot [CH \cdot OH]_2 \cdot CH \cdot O \cdot \overset{|}{C}—CH \cdot [CH(OH)]_2 \cdot CH_2 \cdot OH.$$
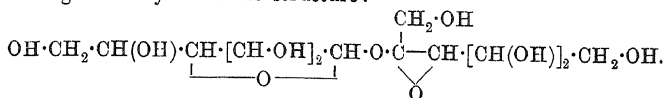
When sucrose is hydrolysed in the presence of acids, these forms are the first to be produced, but subsequently they rapidly undergo isomeric changes, giving successively the corresponding butylene-oxide form of fructose and then an equilibrium mixture of the α- and β-modifications of this, whilst alongside the β-butylene-oxide form of glucose with small amounts of the γ- or ethylene-oxide form of this sugar are produced. On these assumptions, the rotation and low crystallising power of invert-sugar are explained by the complexity of the mixture. Some evidence in favour of this is afforded [51] by contrasting the reducing powers of sucrose while undergoing inversion by (a) invertase and (b) dilute acid by measurements of the time taken to decolorise permanganate, but the formula given above is well substantiated by further investigation by Haworth [52] of the cleavage products of methylated sucrose. In previous investigations, the separation of the cleavage products of octamethyl sucrose was difficult, but heptamethyl sucrose is easily prepared, and, on hydrolysis with dilute hydrochloric acid, yields a trimethyl glucose and a tetramethyl fructose, which are readily separated by fractional distillation under a very low pressure. The trimethyl glucose was characterised by further methylation, which gave tetramethyl α-glucose. The tetramethyl fructose decolorised permanganate, behaved generally as a γ-sugar, and, when oxidised by nitric acid, gave an anhydro-acid or semi-lactide, the analysis of which agreed with an empirical formula, $C_{16}H_{80}O_{11}$. A closely reasoned argument shows that the properties of this point to its formation from an α-hydroxy-acid, which in turn could only be formed from the tetramethyl fructose having the formula

$$OMe \cdot CH_2 \cdot C(OH) \cdot CH \cdot CH(OMe) \cdot CH(OMe) \cdot CH_2 \cdot OMe.$$
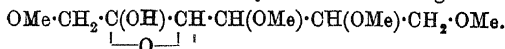
[51] E. F. Armstrong and T. P. Hilditch, T., 1920, 117, 1086.   [52] Ibid., 199.

The extensive study of the alkylated sugars, with which the names of Purdie, Irvine, and Haworth are mainly associated, has obviously opened out a general method for the determination of the constitution of the di- and poly-saccharides, for now that the properties and structures of a large number of alkylated aldoses and ketoses are known, the substances formed in the degradation of polysaccharides may be identified. The original method of alkylation by means of silver oxide and alkyl iodide is not always successful, owing to experimental difficulties, often caused by the insolubility of the carbohydrate in the alkyl iodide, but now that the alternative method of methylation is available in the use of methyl sulphate and sodium hydroxide rapid progress has been made. An investigation of the constitution of the polysaccharides by means of their hydrolysis must include the identification of (1) the constituent sugars, (2) their stereochemical form, (3) the hydroxyl groups involved in the coupling of the constituents, and (4) the position of the internal oxygen ring in each sugar. These methods have now been applied with considerable success to the elucidation of the structure of inulin,[53] and of the conversion of cellulose into glucose.[54]

Inulin, being soluble in aqueous sodium hydroxide, is readily methylated by methyl sulphate to dimethyl inulin, which has the advantageous property of being soluble in methyl iodide. Exhaustive methylation, however, by silver oxide and methyl iodide showed that the formation of trimethyl inulin represented the limit of the reaction. The hydrolysis of this at 100° with 1 per cent. oxalic acid proceeded quite smoothly, and yielded a trimethyl fructose, which, in view of its strong reducing properties, was undoubtedly a member of the γ-, that is, the supposed ethylene-oxide, series of ketoses. The trimethyl fructose was then converted into the corresponding trimethyl fructosides, which, on further methylation and subsequent hydrolysis, yielded the tetramethyl γ-fructose obtained by Haworth[55] from sucrose. The diagram on p. 67 illustrates the great advances made recently in our knowledge of the structural relationship of the four compounds.

The yields obtained in the conversion of inulin to trimethyl γ-fructose show that it is an aggregate of γ-fructose residues, each ketose molecule having lost two hydroxyl groups in the formation of the polysaccharide.

Further deductions from this research suggest one of two alternative formulæ for inulin, which undoubtedly has a smaller

[53] J. C. Irvine and (Miss) E. S. Steele, *T.*, 1920, **117**, 1474.
[54] J. C. Irvine and C. W. Soutar, *ibid.*, 1489.
[55] *Loc. cit.*, see p. 65.

Inulin	→	Fructose	←	Sucrose	→	Glucose
↓		↓		↓		↓
Dimethyl inulin		Tetra-acetyl fructose		Heptamethyl sucrose		Methyl-glucoside (α or β)
↓		↓		↓		↓
Trimethyl inulin		Tetra-acetyl methyl-fructoside		Trimethyl glucose →		Tetramethyl methyl-glucoside
↓		↓		and		↓
Trimethyl γ-fructose		Methyl-fructoside		Tetramethyl γ-fructose		Tetramethyl α-glucose
↓		↓				
Trimethyl γ-methyl-fructoside		Tetramethyl methyl-fructoside				
↓		↓				
Tetramethyl γ-methyl-fructoside		Tetramethyl-fructose				

molecular weight than that given in the literature, and developments of the investigation will be looked for with great interest.

The conversion of cellulose into glucose has been studied by many workers, but not in a strictly quantitative manner, for as Irvine and Soutar point out, the evidence of specific rotation and reducing power, even when apparently consistent, cannot be held to characterise an uncrystallisable syrup as a definite sugar. Some advance has been made in a recent paper by K. Hess and W. Wittelsbach [56] on the acetolysis of ethyl cellulose, but in all work on the hydrolysis of cellulose where a yield of glucose even approximating to the theoretical amount has been claimed, in no case have the results been based on the quantity of a crystalline sugar or of a characteristic derivative actually isolated. The St. Andrews results now described have given, by the degradation of a purified cotton cellulose, a yield of crystalline derivatives of glucose equivalent to 85 per cent. of the theoretical amount. The method consisted in treatment of the cellulose with acetic anhydride and sulphuric acid, after which the soluble and insoluble products were converted into methylglucoside. The methylglucoside obtained was quite free from any isomeric methylhexoside, so that

[56] *Zeitsch. Elektrochem.*, 1920, **26**, 232 ; *A.*, i, 532.

mannose and galactose residues are not present in cellulose. The results point to the following formula for cellobiose,

$$OH\cdot CH\cdot [CH\cdot OH]_2\cdot CH\cdot CH\text{---}O\text{---}CH\cdot [CH\cdot OH]_2\cdot CH\cdot CH(OH)\cdot CH_2\cdot OH$$
$$\underline{\quad\quad O\quad\quad}\quad \dot{C}H_2\cdot OH\quad \underline{\quad\quad O\ \cdots\ }$$
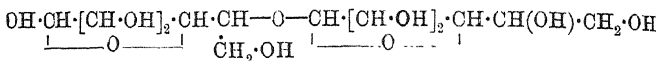
and afford some evidence of the structure of a portion of the cellulose molecule.

Nitrogen Compounds.

The catalytic formation of amines by the Sabatier process is usually unsatisfactory, owing to the difficulty of separating the mixture of primary and secondary amines generally formed. A. Mailhe[57] has, however, shown that the hydrogenation of ketazines in the presence of reduced nickel can be used for the preparation of primary amines if the reaction is carried out at specially low temperatures (about 130°), higher temperatures converting ketazines, and even the low temperatures aldazines,[58] into mixtures of primary and secondary amines. On the other hand, catalytic methods appear to be very convenient for the preparation of certain aliphatic and aromatic nitriles,[59] which are formed when vapours of the esters and ammonia are passed over aluminium or thorium oxide heated to 480—500°. The quantitative formation of hydrogen cyanide when carbon monoxide and ammonia are passed over thoria heated at 430° is a reaction which may become of considerable importance.

A very easy method of preparing guanidine is described by E. A. Werner and J. Bell,[60] who show that commercial dicyanodiamide is depolymerised at 120° in the presence of ammonium thiocyanate, giving an 80 per cent. yield of guanidine thiocyanate.

The α-methyl and α-ethyl derivatives of hydroxylamine[61] are obtained by the prolonged treatment of the corresponding disulphonic acids with concentrated sulphuric acid. The potassium salts of these acids, $RO\cdot N(SO_3K)_2$, are formed by the reactions between alkyl iodides and aqueous solutions of potassium hydroxylaminedisulphonate, and in general, like the potassium salts of the alkylimidosulphonates,[62] $NR(SO_3K)_2$, are noteworthy on account of their sparing solubility in water; thus potassium ethylene-

[57] Compt. rend., 1920, 170, 1265; A., i, 475.   [58] Ibid., 1120; A., i, 475.

[59] Ann. Chim., 1920, [ix], 13, 226; A., i, 476

[60] T., 1920, 117, 1133.

[61] W. Traube, H. Ohlendorf, and H. Zander, Ber., 1920, 53, [B], 1477; A., i, 717.

[62] W. Traube and M. Wolff, ibid., 1493; A., i, 716.

diamine-NN'-tetrasulphonate dissolves only to the extent of 0·2 gram in 100 c.c. of water at the ordinary temperature, whilst the corresponding barium dipotassium is practically insoluble.

A convenient method [63] of preparing cyanogen chloride on a laboratory scale is the action of chlorine on a 12 per cent. solution of hydrogen cyanide. It has been shown that the reaction proceeds quantitatively according to the equation $Cl_2 + HCN = CNCl + HCl$. The pure substance does not undergo polymerisation, but in the absence of water hydrogen chloride causes the slow formation of cyanuric chloride. ROBERT H. PICKARD.

PART II.—HOMOCYCLIC DIVISION.

Theoretical.

THE determination of the energy of atomic linkings in carbon compounds is intimately connected with that of the distribution of valency, and of all the available methods which can assist in throwing further light on these problems, it is probably the thermochemical that is most free from pitfalls in the domain of theory. Considerable progress has been made in the interpretation of the data supplied by the heats of combustion of hydrocarbons. Weinberg [1] points out that the heats of combustion of saturated hydrocarbons can be very nearly expressed by assuming that each carbon atom and each hydrogen atom contributes a constant quantity independent of the constitution. On this hypothesis, the heats of combustion of ethane and propane show that each carbon contributes 96·5 Cal. and each hydrogen 29 65 Cal. Again, from the known increment for each ·CH_2· and from the average heats of combustion of the octanes, the respective values 96 and 30 are obtained. The conclusion is drawn that the energies of rupture of C–H and C–C bonds do not materially differ, and although there seems to be a loophole in this part of the argument, interesting results follow from the application of the additive hypothesis to the case of the unsaturated hydrocarbons. The value calculated from the number of carbon and hydrogen atoms in the molecule subtracted from the observed heat of combustion gives a measure of the additional energy due to the unsaturated linkings. For a single ethylene bond, the increment thus obtained is about 30, or

[63] T. S. Price and S. J. Green, *J. Soc. Chem. Ind.*, 1920, **39**, 98T; *A.*, i, 425.
[1] A. von Weinberg, *Ber.*, 1919, **52**, [B], 1501; *A.*, ii, 14.

15 for each unsaturated carbon atom. For the conjugated $\Delta^{\beta\delta}$-hexadiene the increment is not 60, but only 16·3, and this is justifiably regarded as the increase due to the mutually restricted oscillation of three pairs of unsaturated atoms. If, then, the view of Thiele, that benzene contains three conjugated double bonds, is correct, we have to do with six pairs of unsaturated atoms, and the increment should be 32·6. Actually, it is 32·7 or 30·3, according as the value for the heat of combustion of benzene determined by Roth and Wallasch[2] or by Richards and Barry,[3] respectively, is accepted. It should be pointed out that the above argument might well be reversed, since most chemists will be ready to admit the cyclic conjugation of the benzene molecule, and if the latter is represented by the formula I, then it would seem that $\Delta^{\beta\delta}$-hexadiene should be represented by the expression II.   In

Me·C   CH

Me·C =CH

(I.)   (II.)
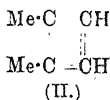
this way, the striking analogies between the properties of certain compounds containing conjugated double bonds and others of true aromatic type might receive some explanation. From the above, it will be seen that the energy of each carbon atom in benzene is about 5 Cal. above the normal for the carbon atom of a paraffin, whilst in ethylene the increment is 15 for each carbon atom. It is therefore particularly striking that in naphthalene and anthracene this increment per carbon atom is also about 5 Cal. Accordingly, all the carbon atoms in these polynuclear hydrocarbons are in a similar condition of unsaturation, and we are led to postulate complete cyclic conjugation in these cases also. The ortho-quinonoid formula for anthracene (III) which Auwers[4] deduces from his observations of the exaltation of the refractive and dispersive powers of 9-*iso*amylanthracene becomes IV if complete conjugation is assumed. There is nothing in the experiments which militates against this view, although a decisive argument is furnished against the adoption of the old idea of a central para-linking, since dihydroanthracenes behave optically exactly as if they contained two normal benzene nuclei.

(III.)   (IV.)
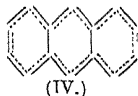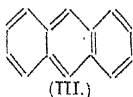
[2] *Annalen*, 1915, **407**, 134; *A.*, 1915, ii, 146.
[3] *J. Amer. Chem. Soc.*, 1915, **37**, 993; *A.*, 1915, ii, 421.
[4] K. von Auwers, *Ber.*, 1920, **53**, [B], 941; *A.*, i, 540.

Fajans[5] has developed a formula for the calculation of the heats of combustion and of formation of hydrocarbons from a more fundamentally sound point of view than that of Weinberg, but the chief interest of his work in relation to the present subject lies in the applications of his methods by Steiger[6] and by Hückel.[7] The former shows that the energy of the C–C linkings in graphite and in aromatic hydrocarbons is almost identical, and draws the conclusion that there is a close analogy in the arrangement of the carbon atoms and in the subdivision of their valencies in the molecules of all these substances. The latter has employed the considerations developed by Fajans and by Steiger to the determination of the energy of polymethylene rings, in order to compare the results with those which might be anticipated from Baeyer's theory. The value for $\cdot CH_2 \cdot$ in open chains is known to be 158 Cal., and the abnormal energy of polymethylenes can therefore be very simply estimated by dividing the heat of combustion by the number of carbon atoms, and comparing the value for the polymethylene $\cdot CH_2 \cdot$ thus obtained with the normal. In this manner, the values 170, 168·5, 165·5, 159, 158 are obtained for the methylene group in ethylene, cyclopropane, cyclobutane, cyclopentane, and cyclohexane respectively. These results are in general agreement with the strain theory, but the values obtained for even such simple derivatives as the methylpolymethylenes and also for cycloheptane require further elucidation.

Sidgwick[8] has passed in review the boiling points of a very large number of position-isomeric benzene derivatives, and has pointed out some hitherto unrecognised regularities and certain interesting exceptions. The derivatives of benzene may be roughly divided into two classes, the normal, in which the boiling points of isomeric ortho-, meta-, and para-compounds do not differ by much more than 10°, and the abnormal, in which the difference is more than 10°, and usually from 20—80°. In the normal series the substituents are of the unchangeable type, and may be alkyl (not aryl), alkyloxy-, or ester groups. In the abnormal series the boiling points of the meta- and para-derivatives are fairly close together, whilst the ortho- is much lower; the substituents here are of a reactive type, such as hydroxyl, carboxyl, amino-, and nitroxyl. These relations extend to the solubilities in water, so far as they have been observed. The isomerides in a normal series exhibit similar solubilities, whereas in abnormal compounds

[5] K. Fajans, *Ber.*, 1920, **53**, [B], 643; *A.*, ii, 354.
[6] A. L. von Steiger, *ibid.*, 666; *A.*, ii, 355.
[7] W. Hückel, *ibid.*, 1277; *A.*, i, 603.
[8] N. V. Sidgwick, *T.*, 1920, **117**, 389.

this is not the case; and where one of the substituents is hydroxyl, the unexpected result is noted that the ortho-derivative is far less readily soluble in water than the meta- or para-derivatives.

A good example of an abnormal series is that of the nitro-phenols. *o*-Nitrophenol boils about 80° lower than the *m*- and *p*-nitrophenols, and it is also much less readily soluble in water. The chlorides of the phthalic acids are anomalous, having the boiling points: *o*-, 281°; *m*-, 276°; *p*-, 259°. If the explanation is that the ortho-derivative has a ring structure, as seems quite probable on chemical grounds, then this view should logically be extended to the meta-derivative also, and the work of von Braun (see below) removes much of the prejudice which might have been felt against such an assumption. In almost all cases a para-compound boils at a higher temperature than the isomeric meta-derivative, but in eleven series in which this rule is reversed one of the substituents is always amino- or substituted amino-. This indicates a constitutional peculiarity for which no explanation is as yet forthcoming.

Some interesting work has been carried out on the influence of nitro-groups on the reactivity of substituents in the benzene nucleus. Kenner and Parkin[9] studied the action of ammonia and of sodium methoxide on 2:3-, 3:4-, and 2:5-dinitrotoluenes, and explain their results in terms of a hypothesis which may be briefly stated in the following propositions: (*a*) Meta-directive groups activate substituents in the ortho- and para-positions, and ortho-para-directive groups have a similar effect on those in the meta-position. (*b*) The displacement of mobile substituents depends primarily on the formation of a molecular additive compound which undergoes rearrangement or decomposition leading to the reaction product. (*c*) The group responsible for the formation of the additive compound is not itself displaced. (*d*) Steric hindrance may be the orientating factor in a displacement by affecting the initial process of addition. This is a some-what complex hypothesis, and it is unfortunate that it appears to be necessary to have recourse to that most unsatisfactory of expedients, steric hindrance, but the facts are certainly difficult to reconcile with a more simple explanation. In 2:3-dinitro-toluene, for example, it is the 2-nitroxyl which is displaced, and this is explained by assuming that steric hindrance prevents the 2-nitro-group from partaking in the formation of an additive product which occurs by the agency of the 3-nitro-group, and therefore the 2-nitro-group is displaced. With 3:4-dinitro-toluene, however, the activating influence of the ortho-para-direc-

[9] J. Kenner and M. Parkin, *T.*, 1920, **117**, 852.

tive methyl group is able in the absence of steric hindrance to be the deciding factor, and the nitroxyl in the 3-position is displaced. The experiments of Holleman and his collaborators [10] on the displacement of groups in the dichloronitrobenzenes and chlorodinitrobenzenes are examined from this point of view, and the results are, in the main, shown to be in good accord with the theory. During the present year the latter work has been extended [11] to the eleven dichlorodinitrobenzenes, and by means of a qualitative and quantitative study of the action of sodium methoxide on these isomerides several interesting points have been illustrated. The activity of a nitro-group, for example, is found to be strengthened by the introduction of a chlorine atom in the meta-position.

Kenner and Parkin give good reasons (loc. cit.) for rejecting the theory that the intermediate products postulated have a quinonoid structure, but there is at least one case, the displacement of nitroxyl by methoxyl in s-trinitrobenzene, in which the existence of a quinonoid intermediate stage is the simplest assumption which can be made to explain an otherwise anomalous reaction.

There are a number of cases in the literature of substances which may have a chain connecting the meta-positions in the benzene nucleus, but Braun and his collaborators have now prepared a series of substances which undoubtedly contain such ring systems and of a type which has hitherto been deemed incapable of existence. The first example was a heterocyclic substance obtained by the reduction of julolidine methochloride,[12] and this was followed [13] by the observation that m-xylylene dicyanide on reduction by means of sodium and alcohol yields as the main product the saturated secondary amine (V) in which the C_2H_4-group may have the ethylene or ethylidene arrangement. The quaternary dimethylammonium hydroxide obtained from it in the usual manner loses water and dimethylamine on distillation, furnishing the unsaturated hydrocarbon (VI), which may be reduced

(V.)   (VI.)   (VII.)
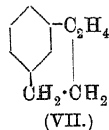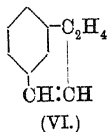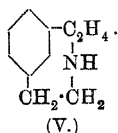
[10] Rec. trav. chim., 1915, 35, 1; A., 1916, i, 22.
[11] A. F. Holleman and A. J. den Hollander, ibid., 1920, 39, 435; A., i, 539.
[12] J. von Braun and L. Neumann, Ber., 1919, 52, [B], 2015; A., i, 87.
[13] J. von Braun, (Frl.) L. Karpf, and W. von Garn, ibid., 1920, 53, [B], 98; A., i, 251.

by means of hydrogen in the presence of colloidal palladium to the saturated hydrocarbon (VII).

All three substances are converted by oxidation into *iso*phthalic acid. The two hydrocarbons have characteristic odours and abnormally low densities. This significant discovery is certain to stimulate numerous further investigations.

Statements at variance with the current stereochemical doctrine are prone to be regarded with suspicion, and perhaps more particularly when made in connexion with the chemistry of cinnamic acid and its isomerides, for in few branches of research has it been so frequently necessary to correct or reinterpret published experiments. It is now claimed [14] that on fusing cinnamic anhydride with tartaric acid, cinnamates are formed which "induce" optical activity in a portion of the cinnamic acid, so that optically active cinnamic acid may be extracted from the fusion by means of light petroleum. If the fact be as stated we may well accept the theory, but much more evidence is needed as to the homogeneity of the optically active material. An interesting asymmetric synthesis of a novel type is that of *l*-menthyl *d*-phenyl-*p*-tolylacetate, which is obtained by the interaction of *l*-menthol and phenyl-*p*-tolylketen in ethereal solution.[15] This represents one of the simplest and least unexceptionable examples of asymmetric synthesis which has been placed on record.

The two stereoisomeric forms of the enolic modification of ethyl phenylpyruvate, and also the ketonic modification, have now been prepared.[16] The solid enol (α: m. p. 51—52°) is that which was already known.[17] On distillation it is slowly changed into a more stable liquid enol (β), and this by the action of sodium acetate becomes the ketonic modification (γ: m. p. 79°).

$$\begin{array}{ccc} H \cdot C \cdot Ph & Ph \cdot C \cdot H & \\ HO \cdot C \cdot CO_2Et & HO \cdot C \cdot CO_2Et & CH_2Ph \cdot CO \cdot CO_2Et \\ \alpha. & \beta. & \gamma. \end{array}$$
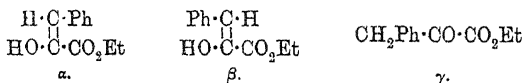
The α- and β-isomerides are readily brominated at $-15°$, and yield a dibromide which rapidly loses hydrogen bromide at the ordinary temperature with the formation of ethyl phenylbromopyruvate. The concordance between theory and practice is complete, especially since the γ-form can be brominated only in boiling carbon disulphide, and then yields a complex product.

[14] E. Erlenmeyer and G. Hilgendorff, *Biochem. Zeitsch.*, 1920, **103**, 79; *A.*, i, 615.

[15] R. Weiss, *Monatsh.*, 1919, **40**, 391; *A.*, i, 555.

[16] H. Gault and R. Weick, *Compt. rend.*, 1920, **171**, 395; *A.*, i, 675.

[17] J. Bougault, *ibid.*, 1914, **158**, 1424; *A.*, 1914, i, 839; J. Bougault and (Mlle) R. Hemmerlé, *ibid.*, 1915, **160**, 100; *A.*, 1915, i, 78.

There is very little real progress to record in connexion with the problem of the relation of colour to constitution, perhaps because the most active workers in this field are devoting their energies to the solution of those more fundamental difficulties which their earlier investigations disclosed. Among those who apply the organic chemist's instinct to this subject Kauffmann is prominent, and the development of his views will be followed with sympathetic interest. A communication [18] which is characteristic of the author's point of view contains an account of the theory of the colour of triphenylcarbinol salts based on the hypothesis of divisible valency, and also a description of experiments made to illustrate the point that basic function and colour-producing function of auxochromes do not run on parallel lines. The isomeric dimethoxybenzaldehydes (2:5-, 3:4, and 2:4-) were condensed with a series of substances containing a reactive methylene group such as nitromethane, phenylacetonitrile, and diketohydrindene, and in all cases it was found that the resorcinol derivative was most basic and least coloured, whilst the quinol derivative was least basic and most coloured and the catechol derivative occupied an intermediate position. It may be noted in passing that the colourless triamino-triphenylmethyl cyanide prepared from pararosaniline and potassium cyanide passes into a coloured dissociating cyanide under the influence of the light of an iron arc.[19]

Turning to the subject of reaction mechanism, it is certainly noteworthy, although not at all surprising, that certain unsaturated hydrocarbons containing conjugated ethylene linkings can combine with negatively substituted diazonium salts with the formation of normal azo-compounds.[20] Thus the compound

$$CH_2 \text{:} CMe \cdot CMe \text{:} CH \cdot N_2 \cdot C_6H_4 \cdot NO_2$$
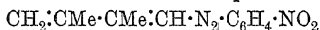
is readily obtained from dimethylbutadiene and p-nitrobenzene-diazonium chloride in glacial acetic acid solution. Curiously enough, it may be reduced by means of tin and hydrochloric acid to a corresponding aminohydrazo-derivative. The occurrence of this coupling reaction is held to support the view that diazo-salts react with aromatic compounds by virtue of an addition to a conjugated system of double bonds. This will be readily admitted, but, in view of the enormously greater readiness with which the reaction occurs in the case of phenols and amines, it seems reasonable to include the unsaturated oxygen or nitrogen atoms in the conjugated system. In this way, too, the theory of Karrer,[21] that

[18] H. Kauffmann, Ber., 1919, 52, [B], 1422; A., i, 50.
[19] I. Lifschitz and C. L. Joffé, ibid., 1919; A., i, 95.
[20] K. H. Meyer and V. Schoeller, ibid., 1468; A., i, 97.
[21] Ibid., 1915, 48, 1398; A., 1915, i, 1073.

addition occurs at the oxygen of phenols or their ethers and at the nitrogen of aromatic amines, is satisfactorily brought into line, and the numerous cases of hydrolysis of phenol ethers during coupling become explicable.

Various Reactions and Synthetical Methods.

Halogenation.—Chlorine may be introduced into the side-chain of toluene and certain derivatives by treating these substances with aqueous hypochlorous acid at temperatures below 0°.[22] It is possible to prepare in this manner benzyl chloride, benzylidene chloride, chlorobenzyl chloride (but not dichlorobenzyl chloride), xylyl chloride, and tolylidene chloride.

Aromatic nitro-compounds when heated with bromine to a high temperature in sealed tubes are changed in many cases to corresponding bromo-derivatives which often suffer further bromination.

The reaction[23] is not a novel one, but has not been employed to any considerable extent as an instrument of research. Many fresh examples are recorded, and advantage is taken of the process to demonstrate that the crude nitration product of anthraquinone contains in all probability the 1 : 2- and 1 : 3-dinitroanthraquinones. Following up the clue, the 1 : 3-isomeride has actually been isolated from the reaction mixture.[24]

Sulphonation.—Iodine is a powerful catalyst in sulphonation, and, for example, it is claimed that an excellent yield of *o*-sulphobenzoic acid is obtained from benzoic acid.[25] The catalyst has, therefore, a definite orientating effect.*

Quinol[26] reacts with aqueous sodium hydrogen sulphite at 100° with the formation of sodium *cyclo*hexane-1 : 4-diol-1 : 2 : 4-trisulphonate, whilst resorcinol[27] under the same conditions is changed to a substance which appears to be the sodium bisulphite compound of *cyclo*hexane-3 : 5-dionesulphonic acid.

Nitration.—The intensely coloured by-product obtained in the nitration of thymol ethyl ether was first isolated by Kehrmann

[22] Levinstein, Ltd., H. Levinstein, and W. Bader, *Brit. Pat.* 134250; *A.,* i, 21.

[23] S. N. Dhar, *T.*, 1920, 117, 993.   [24] *Ibid.*, 1001.

[25] J. N. Rây and M. L. Dey, *ibid.*, 1405.

* Mr. J. Ogilvie, who has repeated the experiment of the sulphonation of benzoic acid under the conditions prescribed in this paper, reports that he is able to confirm the catalytic effect of iodine in the reaction. On alkali-fusion of the product, however, *m*-hydroxybenzoic acid (m. p. 199—200°) was produced, and there was no evidence of the formation of salicylic acid.

[26] W. Fuchs and B. Elsner, *Ber.*, 1919, 52, [B], 2281; *A.,* i, 159.

[27] *Ibid.*, 1920, 53, [B], 886; *A.,* i, 545.

and Messinger,[28] and later studied by Decker and Solonina,[29] who regarded the substance as a quinonoid anhydro-salt of dicymyl-hydroxylamine N-oxide. The discovery that in many cases the perchlorates of these bases can be readily isolated has led to more extended investigations [30] embracing the action of nitric acid on other phenol ethers. The nitration product of anisole, added to perchloric acid, gives a crystalline precipitate of the perchlorate (VIII), and this may be reduced to di-p-anisylamine, or by very gentle treatment to di-p-anisylnitric oxide (IX).

$$\text{OMe·C}_6\text{H}_4\text{·N(:O):C}_6\text{H}_4\text{:O}\!<^{\text{Me}}_{\text{ClO}_4} \qquad \text{NO(C}_6\text{H}_4\text{·OMe)}_2$$
$$\text{(VIII.)} \qquad\qquad\qquad \text{(IX.)}$$
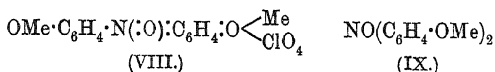
The quinonoid perchlorate yields solutions which are pure blue in thin layers and red in deep layers. The nitric oxide has the appearance of copper powder, and is much more stable than the corresponding diphenyl derivative,[31] and this is remarkable, since di-p-tolylnitric oxide is less stable than the latter substance.

Replacements.—The direct conversion of bromobenzene into benzoic acid, p-dibromobenzene into terephthalic acid, p-bromo-aniline into p-aminobenzoic acid, and similar transformations in the benzene, naphthalene, and thiophen series, may be accomplished by the action of aqueous or aqueous alcoholic potassium cyanide in the presence of cuprous cyanide at 200°.[32]   Although copper is the unique catalyst in this reaction, and also in the displacement of halogen directly attached to the nucleus by hydroxyl or amino-groups, other elements or their compounds may be of practical service in effecting the transformations of diazonium compounds. Thus the double cyanide of nickel and potassium may be used for the preparation of nitriles by the Sandmeyer method with good results,[33] and cobalt thiocyanate is an excellent catalyst for the conversion of diazonium salts into the corresponding thiocyanates. Nickel and cobalt salts are, however, ineffective in the preparation of halogen derivatives through the diazonium salts.

Aromatic acids may in certain cases be reduced to aldehydes via their anilides and related phenyliminochlorides. These are converted by stannous chloride in ethereal solution into the tin double

[28] *Ber.*, 1901, **34**, 1626; *A.*, 1901, i, 484; compare F. Kehrmann, *Ber.*, 1919, **52**, [B], 2119; *A.*, i, 156.

[29] *Ibid.*, 1902, **35**, 3217; *A.*, 1902, i, 767.

[30] K. H. Meyer and H. Gottlieb-Billroth, *ibid.*, 1919, **52**, [B], 1476; *A.*, i, 37.

[31] H. Wieland and M. Offenbächer, *ibid.*, 1914, **47**, 2111; *A.*, 1914, i, 955.

[32] K. W. Rosenmund and E. Struck, *ibid.*, 1919, **52**, [B], 1749; *A.*, i, 44.

[33] A. Korczyński, W. Mroziński, and W. Vielau, *Compt. rend.*, 1920, **171**, 182; *A.*, i, 643.

salts of Schiff's bases, which may be hydrolysed, and good yields of the aldehydes are so obtained.[34]   Benzaldehyde, cinnamaldehyde, p-hydroxybenzaldehyde (starting from p-ethylcarbonatobenzoic acid), and 3 : 4 : 5-trimethoxybenzaldehyde have been prepared in this way.

Friedel-Crafts Reaction.—The action of cyanogen bromide on various aromatic substances in the presence of aluminium chloride has been further investigated [35] and good results have been obtained, especially with the phenol ethers, which are converted into nitriles. The method will be serviceable in those cases where the corresponding hydroxy-acid is not conveniently prepared by the usual methods, such as the Kolbe synthesis and the action of bicarbonates on the polyhydric phenols.   Cyanogen chloride gives the same products as the bromide, and is almost equally reactive.

A modification of the Friedel-Crafts reaction has been described,[36] and consists essentially in the employment of an aromatic hydrocarbon with aluminium powder and excess of mercuric chloride.   It is thought that the reaction proceeds in accordance with the equation

$$C_6H_6 + Al + 2HgCl_2 = C_6H_5AlCl_2 \cdot HgCl + Hg,$$
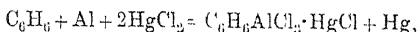
and the large excess of mercuric chloride is designed to avoid the production of mercury.   Using this product as catalyst, a number of remarkable results have been obtained.   For example, thianthren is prepared from benzene and sulphur in a yield of 85 per cent. of that theoretically possible.

Closely associated with the Friedel-Crafts reaction in performance, although not in theory, is Hoesch's synthesis, which, it will be recalled, is based on the production of the ketimine hydrochlorides by the condensation of nitriles with phenols by hydrogen chloride in the presence of anhydrous zinc chloride and ether. Hydroxy- and methoxy-acetonitriles have now been employed in this reaction, and condensed with such phenols as resorcinol and its methyl ether and phloroglucinol.   In some cases, the use of zinc chloride is found to be unnecessary, and a 94 per cent. yield of ω-methoxyresacetophenone is obtained by hydrolysing the initial product of the condensation of methoxyacetonitrile and resorcinol in ethereal solution by means of hydrogen chloride.[37]

Formaldehyde Condensations.—The usual assumption is that the condensation of formaldehyde with aniline and its derivatives, with

[34] A. Sonn and Ernst Müller, *Ber.*, 1919, **52**, [B], 1927; *A.*, i, 58.

[35] P. Karrer, A. Rebmann, and E. Zeiler, *Helv. Chim. Acta*, 1920, **3**, 261; *A.*, i, 389.   [36] J. N. Rây, *T.*, 1920, **117**, 1335.

[37] W. K. Slater and H. Stephen, *ibid.*, 309.

the formation of substituted diphenylmethanes, occurs exclusively in the para-position with respect to the amino-group. This is erroneous, and the product from dianilinomethane or from anhydroformaldehydeaniline and aniline is a mixture of 4:4'- and 2:4'-diaminodiphenylmethanes in the proportions of approximately nine to one.[38] Examination of the nitro-derivatives of the crude product supplied the first clue, and methods were later evolved for the actual separation of the constituents of the mixture. The production of 2:4'-diaminodiphenylmethane (X) in this condensation is paralleled by that of diaminophenylacridine (XI) in the magenta fusion.
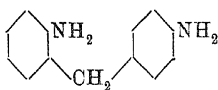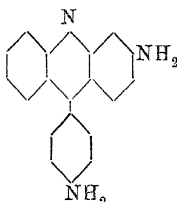
(X.) (XI.)

A careful study of the conditions of condensation of chloromethyl ether and dichloromethyl ether with aromatic compounds has led to the elaboration of a novel method for the direct introduction of the chloromethyl group into the aromatic nucleus.[39]

Of the various suggested processes, that which depends on the condensation of the aromatic hydrocarbons with s-dichloromethyl ether in the presence of zinc chloride appears to be the most satisfactory in practice. It is unnecessary to employ highly purified dichlorodimethyl ether, the crude oil from the action of hydrogen chloride on 40 per cent. aqueous formaldehyde being utilisable, and it is even an advantage in some examples to employ the whole crude product without separation of the aqueous layer, and in that case sufficient anhydrous zinc chloride is added ultimately to form $ZnCl_2,2H_2O$. Benzyl chloride, p-xylylene dichloride, p-chlorobenzyl chloride, and other similar substances were successfully prepared, and the reaction is also applicable to the introduction of the bromomethyl group.

The condensation of styrene with formaldehyde yields β-phenyltrimethylene glycol (XII) and its methylene ether. Anethole gives rise to a similar product, whilst camphene in glacial acetic acid solution is changed by trioxymethylene into homocamphenol

[38] H. King, *T.*, 1920, **117**, 988.
[39] H. Stephen, W. H. Short, and G. Gladding, *ibid.*, 510.

acetate.[40]   Homocamphenol or camphenylidene-6-ethanol has been oxidised to the corresponding aldehyde and acid, and numerous derivatives have been prepared.

$$CHPh(CH_2 \cdot OH)_2 \qquad CHPh{:}CH \cdot CH{:}CH \cdot CO \cdot NH_2$$
$$\text{(XII.)} \qquad\qquad\qquad \text{(XIII.)}$$

$$CHPh{:}CH \cdot CH{:}CH \cdot NH \cdot CO_2Me \qquad CHPh{:}CH \cdot CH_2 \cdot CHO$$
$$\text{(XIV.)} \qquad\qquad\qquad\qquad \text{(XV.)}$$
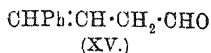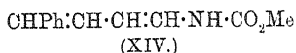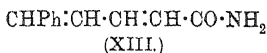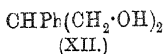
Hofmann Reaction.—It is well known that the Hofmann reaction for the preparation of amines from acid amides does not proceed smoothly with $\alpha\beta$-unsaturated amides, but this is due to the ready hydrolysis of the unsaturated amines into an aldehyde and ammonia.   Experimental details have now been recorded[41] applicable to the control of this process, and enabling the final product to be isolated.   To take an example, cinnamenylacrylamide (XIII) is treated with sodium hypochlorite in the presence of methyl alcohol, and the product is cinnamenylvinylurethane (XIV), which is hydrolysed by sulphuric acid to β-benzylidene-propaldehyde (XV).   If the process is a reasonably general one, it will have many applications.

Oxidation.—The catalytic oxidation of benzene by gases containing oxygen at temperatures of 300—700° results in the production of *p*-benzoquinone and maleic acid.[42]   The process is clearly of technical interest, and a large variety of catalysts are claimed, but probably none is so effective as the first-named, which is vanadium oxide distributed on pumice.

It is perhaps worth noting, in view of the ever-increasing application of the method of ozonisation, that potassium ferrocyanide reduces many ozonides of unsaturated substances with the minimum formation of tarry by-products.[43]   The constitution of a number of enols has been probed by examining the products of their oxidation by ozone.[44]

The anodic oxidation of benzoic acid introduces hydroxyl groups into the nucleus.[45]   Catechol, quinol, 2:5-dihydroxybenzoic acid, and a hydroxyquinolcarboxylic acid were isolated from the product.

The oxidation of amines still engages attention, and Gold-

[40] H. J. Prins, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 51; *A.*, i, 42; G. Langlois, *Ann. Chim.*, 1919, [ix], **12**, 265; *A.*, i, 241.

[41] I. J. Rinkes, *Rec. trav. chim.*, 1920, **39**, 200; *A.*, i, 322.

[42] J. M. Weiss and C. R. Downs, *J. Ind. Eng. Chem.*, 1920, **12**, 228; *A.*, i, 426.

[43] C. Harries, *D.R.-P.* 321567; *A.*, i, 675.

[44] J. Scheiber and G. Hopfer, *Ber.*, 1920, **53**, [B], 697, 898; *A.*, i, 487, 552.

[45] F. Fichter and E. Uhl, *Helv. Chim. Acta*, 1920, **3**, 22; *A.*, i, 234.

schmidt [46] finds that Bamberger's hypothesis, that phenylhydroxyl-amine is the sole first stage in the oxidation of aniline, is inadequate, since that substance is not sufficiently reactive to explain the formation of the polynuclear oxidation products. An additional first stage is therefore postulated in the bivalent radicle PhN:, which polymerises into azobenzene, benzoquinonephenyldi-imine, $NPh:C_6H_4:NH$, and emeraldine.

By carrying out the oxidation of amines with a free para-position in ether by means of lead peroxide and anhydrous sodium sulphate, azo-compounds and quinonearyldi-imines are produced, and, what is still more interesting, the oxidation of a mixture of amines yields mixed azo-compounds and mixed quinonearyldi-imines. Triphenylhydrazine is oxidised at $-60°$ in methyl ether to hexaphenyltetrazane, $NPh_2\cdot NPh\cdot NPh\cdot NPh_2$, which can be isolated as a green crust, and forms solutions in ether, which are pale greenish-blue at $-80°$, and deep blue at the ordinary temperature. This is probably due to dissociation into the radicle, triphenylhydrazyl, $NPh_2\cdot NPh\cdots$, relatively stable to oxygen, but easily combining with nitric oxide. Wieland and his school have continued the study of the ditertiary hydrazines,[47] but the results, although of great interest, are along the lines of previous work emanating from the same laboratory. Tetrabenzylhydrazine shows no tendency to dissociate, and it appears that this phenomenon is conditioned by the direct attachment of the nitrogen to the nucleus, and that it is intensified when there are ortho-para-directive substituents in the ring.

Unsaturation.

Pinene, nopinene, and γ-pinene have remarkable avidity for hydrogen chloride and hydrogen bromide, so that, especially at elevated temperatures, these hydrocarbons will actually decompose aniline hydrochloride and ammonium chloride, with the formation of the hydrochlorides of the terpenes. Bornyl chloride is also formed by double decomposition between pinene and numerous chlorine-containing terpene derivatives, such as sylvestrene dihydrochloride and camphene hydrochloride.[48] The observation may be of practical, as well as of theoretical, interest, since it would be difficult to devise a more neutral reagent than a terpene, and this is frequently a desideratum in processes which involve the removal of the elements of halogen acids.

[46] S. Goldschmidt, *Ber.*, 1920, 53, [B], 28; *A.*, i, 226, 258.
[47] H. Wieland and E. Schamberg, *ibid.*, 1329; *A.*, i, 768.
[48] O. Aschan, *Öfvers. Finska Vet.-Soc.*, 1916, 58; *A.*, i, 318.

The possible number of polymerides of an unsymmetrical ethylene derivative of the form $aCH{:}CHb$ is very great, even when the dimerides alone are calculated and the constitution is restricted to the possible *cyclo*-butanes and butylenes. Theory indicates two *cyclo*butanes, each existing in four stereoisomeric modifications, and five butylenes, each of which would have *cis*- and *trans*-forms. That is, there are eighteen possibilities, without including the enantiomorphous or racemic modifications. Puxeddu[49] restricts the possible number of polymerides of anethole to eleven, and has now succeeded in isolating the seventh known substance of this type by fractionally distilling in a vacuum, and afterwards crystallising the white precipitate obtained by the addition of ferric chloride to an ethereal solution of the anisylmethylethylene.

At 120—180°, two molecules of isoprene rapidly attack one of *p*-benzoquinone, with the production of a substance, to which the formula XVI has been provisionally assigned.[50] It forms a tetrabromide and dioxime. The reaction is clearly related to the

$$\underset{\text{(XVI.)}}{}\qquad\qquad \underset{\text{(XVII.)}}{\begin{array}{l} CHPh{\cdot}CH_2 \\ \mid\qquad\quad\mid \\ OC\text{——}CPh_2 \end{array}}$$
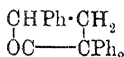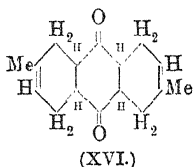
polymerisation of isoprene itself, with the formation of dimethyl*cyclo*octadiene.

A further numerous class of similar reactions are those which involve the formation of *cyclo*butane derivatives from the ketens. Dimerisation of the latter produces *cyclo*butanediones, whereas with ethylene derivatives the addition of ketens yields *cyclo*butanones.[51] Thus styrene condenses with diphenylketen, with production of the compound XVII, and many other examples have been recorded. *cyclo*Pentadiene reacts with one molecule of diphenylketen, whilst *N*-methylpyrrole reacts with two molecules, even when the components are applied in molar proportions. Attempts have been made to prepare the optically active camphorketen, in order to facilitate by polarimetric methods the study of these additive reactions, but only partial success was achieved. The most successful experiments were those on the action of quinoline on camphorcarboxyl chloride. The resulting solution contains the desired product in the free state for a short period,

[49] E. Puxeddu, *Gazzetta*, 1920, **50**, i, 149; *A.*, i, 481.
[50] H. von Euler and K. O. Josephson, *Ber.*, 1920, **53**, [B], 822; *A.*, i, 489.
[51] H. Staudinger and E. Sutor, *ibid.*, 1092; *A.*, i, 556.

but it is very reactive, and quickly passes over into its dimerides. The fact that these were isolated in stereoisomeric modifications is opposed to Schroeter's view that these substances are molecular compounds bound together loosely by partial valencies, and is strong evidence that they are correctly regarded as normal *cyclo*-butane derivatives.[52]

Some extremely suggestive results have been obtained in the course of an investigation of the behaviour of diphenylnitric oxide towards other radicles, such as nitric oxide and triphenylmethyl.[53] Diphenylnitric oxide, $Ph_2N\dot{:}O$, is apparently the analogue of nitrogen peroxide, and when treated with nitric oxide at 0°, the initial product is probably $O\dot{:}NPh_2\dot{\cdot}N\dot{:}O$, which is the analogue of nitrogen trioxide. The products actually isolated are the nitroso-derivatives of diphenylamine and *p*-nitrodiphenylamine, and the mechanism of their production is probably as follows. The hypothetical intermediate isomerises into diphenylnitroamine, $Ph_2N\cdot NO_2$, and then nitrodiphenylamine, $NO_2\cdot C_6H_4\cdot NHPh$, which when produced is immediately nitrosated by the supposed intermediate, in accordance with the scheme:

$NO_2\cdot C_6H_4\cdot NHPh + O\dot{:}NPh_2\dot{\cdot}N\dot{:}O = NO_2\cdot C_6H_4\cdot NPh\cdot NO + NPh_2\cdot OH.$
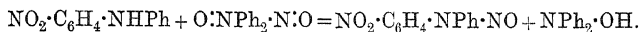
Auto-decomposition of diphenylhydroxylamine produces diphenylamine, which is itself nitrosated according to a similar scheme. That an analogue of nitrogen trioxide is actually produced in this reaction may be proved by performing the process in the presence of a secondary base, such as di-*p*-tolylamine, when large amounts of the related nitrosoamine can be isolated. With triphenylmethyl, diphenylnitric oxide yields the compound XVIII, the initial product being so unsaturated that it unites with a second molecule of the hydrocarbon. The constitution of the substance follows from the products obtained by catalytic hydrogenation. These are diphenylamine and *p*-benzhydryltetraphenylmethane, the nature of which has been elucidated by Tschitschibabin.[54]

$$Ph_2N\cdot O\cdot CPh_2\!\!\diagdown\!\!\diagup CPh_3.$$
(XVIII.)
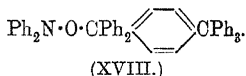
Molecular Rearrangement.

The smooth transformation of *n*-butylaniline into 4-butylaniline by heating with hydrochloric acid or certain metallic chlorides [55]

[52] H. Staudinger and S. Schotz, *Ber.*, 1920, **53**, [B], 1105; *A.*, i, 557.

[53] H. Wieland and K. Roth, *ibid.*, 210; *A.*, i, 304.

[54] *Ibid.*, 1904, **37**, 4709; *A.*, 1905, i, 125.

[55] J. Reilly and W. J. Hickinbottom, *T.*, 1920, **117**, 103.

is of interest, on account of the fact that no rearrangement of the butyl radicle occurs in the process.   It will be recalled that Ladenburg found that propylpyridinium salts gave α-*iso*propyl-pyridine on heating, and there are many similar instances.   The statement in the theoretical discussion of the process that the reaction cannot be satisfactorily explained by assuming the inter-mediate formation of butyl chloride is of doubtful validity, and experimental evidence opposed to the theory of double decomposi-tion and re-synthesis is not put forward.

Attempts during the present year[56] to generalise the Claisen transformation have been quite unsuccessful, and the rearrange-ment of phenolic ethers into substituted phenols on heating appears to be characteristic of the allyl ethers.

β-Naphthyl vinyl ether, which does not undergo the transform-ation, has an intense odour of tangarine skins.[57]

A pinacone–pinacoline type transformation, which involves the conversion of a hydrogenated naphthalene into a hydrindene derivative, is illustrated in the annexed scheme, the reagent employed being silver nitrate in ethereal solution.[58]
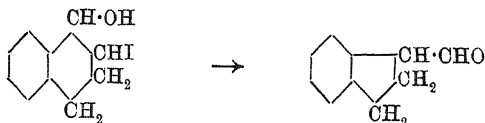
When benzophenoneoxime is warmed with phosphorus penta-sulphide, it yields thiobenzanilide as the result of a Beckmann change. It is now found that the rearrangement is due to the formation of an ester of the thio-oxime, since, if the reaction is carried out in ethereal suspension, thiobenzophenoneoxime hydrogen phosphate, $HO \cdot PO(SN\colon CPh_2)_2$, is obtained, and this changes into thiobenzanilide at 70° with almost explosive violence.[59]

Still another transformation has been discovered which is con-ditioned by, and peculiar to, the allyl group. Methylallylaniline N-oxide, $CH_2\colon CH \cdot CH_2 \cdot O \cdot NPhMe\colon O$, heated in presence of alkali in a current of steam, is converted into N-phenylmethyl-O-allyl-hydroxylamine, $CH_2\colon CH \cdot CH_2 \cdot O \cdot NMePh$.[60]

[56] S. G. Powell and R. Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 646 ; *A.*, i, 381.

[57] J. von Braun and G. Kirschbaum, *Ber.*, 1920, **53**, [B], 1399 ; *A.*, i, 728.

[58] M. Tiffeneau and A. Orékhoff, *Compt. rend.*, 1920, **170**, 465 ; *A.*, i, 313.

[59] M. Kuhara and K. Kashima, *Mem. Coll. Sci. Kyoto*, 1919, **4**, 69 ; *A.*, i, 314.

[60] J. Meisenheimer, *Ber.*, 1919, **52**, [B], 1667 ; *A.*, i, 35.

Natural Products.

Chlorogenic acid, the tannin-like constituent of coffee, has been re-examined,[61] and found to have a relatively simple constitution. It is apparently a depside of caffeic acid and quinic acid, in which the carboxyl group of the caffeic acid assumes the ester function, as shown in the formula:

$$C_6H_3(OH)_2 \cdot CH{:}CH \cdot CO \cdot O \cdot C_6H_7(OH)_3 \cdot CO_2H.$$
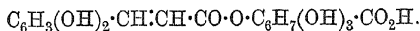
Aspidinol and an isomeric compound, ψ-aspidinol, are obtained by condensation of butyronitrile with methylphloroglucinol β-monomethyl ether in the presence of hydrogen chloride.[62] The two compounds are doubtless the 3- and the 5-butyryl derivatives of the methylphloroglucinol methyl ether, but it is not yet possible to assign one formula or the other to aspidinol. In connexion with the synthesis of plant pigments and other natural products containing the phloroglucinol nucleus, it should be noted that phloroacetophenone, $C_6H_2(OH)_3 \cdot COMe$, can be obtained by the hydrolysis of the pyranol, which is the isolated product of the Nencki condensation applied to phloroglucinol.[63]

The investigation of capsaicin has been continued, and the pungent principle has been regenerated from synthetical vanillyl-amine [64] and decenoyl chloride from the decenoic acid obtained by hydrolysis of capsaicin.[65] There is little remaining doubt that the substance is decenylvanillylamide. As regards the constitution of the acid fragment, a little progress has been possible, since the fusion of this decenoic acid with potassium hydroxide furnishes acetic acid and an octoic acid with a branched chain. This proves that the α-carbon atom is joined only to the carboxyl group and one other carbon atom, but it gives no information relating to the position of the double bond, because it is well known that oleic acid and many of its isomerides yield acetic and palmitic acids on fusion with alkali hydroxides.

The colouring matter of henna leaves, lawsone, has the empirical formula $C_{10}H_6O_3$, and from its chemical behaviour the conclusion is drawn that it is a hydroxynaphthaquinone, and probably identical with 2-hydroxy-1 : 4-naphthaquinone.[66]

The attack on the problem of carminic acid has been resumed,

[61] K. Freudenberg, *Ber.*, 1920, **53**, [B], 232 ; *A.*, i, 322.

[62] P. Karrer and F. Widmer, *Helv. Chim. Acta*, 1920, **3**, 392 ; *A.*, i, 441.

[63] K. B. Sen and P. C. Ghosh, *T.*, 1920, **117**, 61.

[64] E. K. Nelson, *U.S. Pat.* 1329272 ; *A.*, i, 543.

[65] E. K. Nelson, *J. Amer. Chem. Soc.*, 1920, **42**, 597 ; *A.*, i, 380.

[66] G. Tommasi, *Gazzetta*, 1920, **50**, i, 263 ; *A.*, i, 626.

and, largely from analogy to the more closely investigated kermesic acid and the similar behaviour of carminic acid towards reducing and oxidising agents, the formula XIX has been assigned to the substance.[67] Carminic acid is optically active, and the side-chain of unknown constitution is doubtless of sugar-like character; nevertheless, the substance is certainly not a glucoside. It yields an octa-acetyl derivative, and by careful treatment a hexa-acetyl derivative, which may be oxidised by lead tetra-acetate to an unstable diquinone reducible by sulphurous acid. The moderated acetylation of carminic acid therefore leaves two hydroxyl groups in the α-position in the anthraquinone nucleus unaffected.

(XIX.)
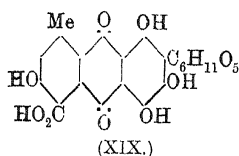
Simonsen[68] has isolated a new dicyclic terpene from the constituents of Indian turpentine from *Pinus longifolia*, Roxb. It has a characteristic, sweet odour, and forms a crystalline nitrosate. On treatment with hydrogen chloride in ethereal solution, it yielded a mixture of *d*-sylvestrene and dipentene hydrochlorides, and this conversion into the meta- and para-series at once suggested the possibility that the hydrocarbon is a carene having one of the formulæ

(A) Δ^3-Carene.　　(B) Δ^4-Carene.　　(C) Dehydrocarane.
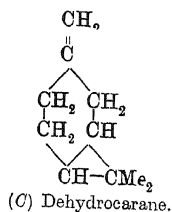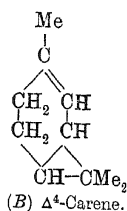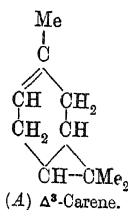
On oxidation by means of potassium permanganate, dimethyl-malonic acid, and, under other conditions, *trans*-caronic acid, were obtained, so that this view was amply confirmed. The molecular refraction was found to be 44·22, which is in good agreement with the calculated value (44·19) for a compound containing a *cyclo*-hexane and a *cyclo*propane ring, and which does not contain conjugated linkings or other causes of optical abnormality. This in

[67] O. Dimroth and H. Kammerer, *Ber.*, 1920, **53**, [B], 471 ; *A.*, i, 442.
[68] J. L. Simonsen, *T.*, 1920, **117**, 570.

itself favours the formula A, and is almost decisive against B. C is improbable, since the glycol obtained by very careful permanganate oxidation does not react with phthalic anhydride in benzene solution, an indication that the group ·CH_2·OH is absent. The terpene is dextrorotatory, and is called d-carene. It is very probably d-Δ^3-carene, and is the first naturally occurring terpene which has been found to contain the carane ring.

Alicyclic Group.

When it is considered how difficult it may be to introduce two alkyl groups into certain esters, for example, ethyl benzoylacetate, which form relatively stable sodium derivatives, it appears remarkable that the alkylation of 2-methyl*cyclo*hexanone by means of methyl or ethyl iodides and sodamide should give rise to 2 : 2-dimethyl*cyclo*hexanone or the corresponding methylethyl derivative respectively.[69] The dialkylated ketones condense with benzaldehyde to form benzylidene derivatives, so that there is no doubt as to the correctness of the constitutions assigned. Considerable improvements have been effected in the technique of the catalytic reduction of aromatic amines,[70] and the conditions can now be regulated so as to obtain either a *cyclo*hexylamine or a di*cyclo*hexylamine as the main product. The catalyst employed is colloidal platinum, of which a rather larger proportion than usual is necessary. Thus, in reducing a monoamine, a catalyst concentration of about 0·6 per cent. is employed, and for a diamine about twice as much. The influence of temperature, concentration, and proportion of hydrochloric acid present in the mixture are all marked. Excellent yields of *cyclo*hexylamine or di*cyclo*hexylamine are obtained from aniline, and the reduction of the toluidines and m- and p-nitroanilines has been effected with equally good results. The methyl*cyclo*hexylamines from the three toluidines are each obtained in stereoisomeric forms, recognised by the production of α- and β-benzoyl derivatives. The new availability of these useful bases will probably provide a further stimulus to the study of partly hydrogenated aromatic hydrocarbons, which are readily obtained from them by applying the process of exhaustive methylation.

A communication of quite outstanding interest is that of Beesley and Thorpe,[71] dealing with the preparation of derivatives of

[69] A. Haller and R. Cornubert, *Compt. rend.*, 1920, **170**, 700, 973; *A*., i, 390, 441.

[70] A. Skita and W. Berendt, *Ber.*, 1919, **52**, [B], 1519; *A*., i, 27.

[71] R. M. Beesley and J. F. Thorpe, *T*., 1920, **117**, 591.

*dicyclo*butane and *tricyclo*butane. A new system of nomenclature of associated alicyclic systems is proposed, and this is capable of accurately expressing in words and symbols the constitutions of the most complex interlocked structures. It is simple and logical, but a shortened exposition would serve no useful purpose, and the original must be consulted. In view of the fact that the introduction of the new nomenclature is a recent event, the compounds mentioned below are described in the ordinary way, the numbering of the *dicyclo*butane ring commencing at the tertiary carbon atom. $\beta\beta$-Dimethylpropanetricarboxylic acid (XX) is converted into the dibromo-ester (XXI), and the latter is found to be changed by concentrated aqueous potassium hydroxide at a high temperature into 1-methyl*dicyclo*butane-2:3:4-tricarboxylic acid (XXII).

$$CMe\!\!\begin{cases} CH_2\cdot CO_2H \\ CH_2\cdot CO_2H \\ CH_2\cdot CO_2H \end{cases} \quad CMe\!\!\begin{cases} CHBr\cdot CO_2Et \\ CHBr\cdot CO_2Et \\ CH_2\cdot CO_2Et \end{cases} \quad CMe\!\!\begin{cases} CH\cdot CO_2H \\ C\cdot CO_2H \\ CH\cdot CO_2H \end{cases}$$

$$\text{(XX.)} \qquad\qquad \text{(XXI.)} \qquad\qquad \text{(XXII.)}$$
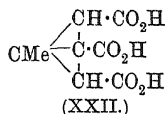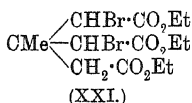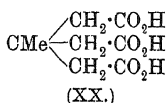
This remarkable compound can theoretically exist in three stereoisomeric modifications, and, in point of fact, three modifications have been isolated, melting at 154°, 193°, and 165° respectively. The first-mentioned readily yields an anhydride, the third does so with greater difficulty, whilst the second shows no tendency whatever to form an anhydride. The carboxyl group in position 3 is found on the models to point away from the system, and, moreover, methyl*tricyclo*butanetricarboxylic acid (see below) shows no tendency to form an˜anhydride, so that this property in the above acids is restricted to the carboxyl groups in positions 2 and 4. On this basis, the three isomerides have the configurations assigned in the following figures:

(M. p. 154°.)   (M. p. 193°.)   (M. p. 165°.)
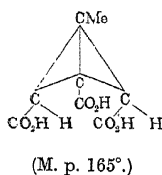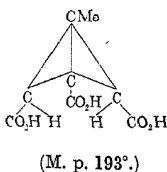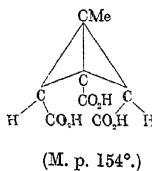
The three acids are formed in approximately equal amount in the original reaction, and are separated by taking advantage of the fact that the acids are insoluble in ether, whilst the two anhydrides are readily soluble in this solvent. The mixture is therefore heated, and the anhydro-acid derived from the *meso-cis*-isomeride (m. p. 154°) extracted. The residue is treated with

acetic anhydride, when the racemic modification (m. p. 165°) is dehydrated, and can be similarly removed, leaving a residue of the *meso-trans*-acid (m. p. 193°). The neatest possible confirmation of the correctness of the assignment of the above formulæ is obtained by studying the behaviour of the three isomerides on bromination. The bromo-triethyl ester from the acid melting at 154° simply yields a stable bromo-acid when hydrolysed, and this harmonises with the configuration, because the bromine atom does not approach the groups in the molecule, with which it can react. The bromo-triethyl ester from the acid melting at 165° yields, on boiling with pyridine, a lactonic ester (XXIII), because in this case the bromine atom is close to a carboxyethyl group. When the acid melting at 193° is treated with phosphorus pentabromide and bromine, and the product poured into alcohol, a bromo-derivative is not formed at all, or, if formed, is too unstable to exist, and by loss of hydrogen bromide passes into an ester of methyl-*tricyclo*butanetricarboxylic acid (XXIV). This, again, accords well with the configuration assigned to the acid melting at 193°.

(XXIII.)   (XXIV.)
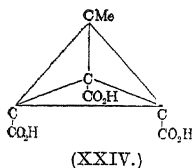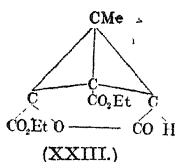
The acid, XXIV, the preparation of which was briefly announced in 1913,[72] may also be obtained in small yield by the action of hot aqueous potassium hydroxide on the tribromo-ethyl ester derived from $\beta\beta$-dimethylpropanetricarboxylic acid (XX). From the structural point of view it is one of the most interesting substances synthesised in recent years, for the tetrahedral arrangement of the four substituents is concentric with that of the four groups attached to a methane carbon atom. The symmetry of methane is reproduced exactly, and enantiomorphism should be possible in this series only when all four groups are different. Again, the tetrahedral unit, C_4, has the arrangement of atoms which is characteristic of the diamond crystal. It is most unfortunate that a group of substances in which so many crucial tests of the soundness of deductions from the models can be applied should be so difficult to prepare in large quantities.

The condensation of ethyl $\alpha\alpha'$-dibromo-$\beta\beta'$-dimethylglutarate with ethyl malonate in presence of alcoholic sodium ethoxide leads

[72] J. F. Thorpe, *P.*, 1913, **29**, 346.

to the formation of a yellow sodium salt, to which the constitution XXV was assigned.[73] On hydrolysis by acids, the monobasic acid XXVI is ultimately obtained, and all the experimental evidence is in agreement with this view of the bicyclic nature of the substances. It is now found that the acid XXVI is produced by the action of boiling dilute alkali hydroxides on $a\delta$-diketo-$\beta\beta$-dimethyl-hexoic acid (XXVII), which is obtained[74] on oxidising dehydro-*iso*fenchoic acid by means of potassium permanganate under special conditions. Too much attention need not be paid to the conclusion drawn from this experiment that the formulæ XXV and XXVI are insufficiently grounded, and that the substances are, in reality, *cyclo*pentene derivatives, because the real existence of the fused *cyclo*propane ring has since been demonstrated in a convincing manner.[75]

$$CMe_2\diagdown \begin{array}{l} C(CO_2Et)\cdot C\!:\!C(ONa)\cdot OEt \\ C(CO_2Et)\cdot CO \end{array}$$

(XXV.)

$$\begin{array}{l} Me_2C\text{-----}C\cdot CO_2H \\ \qquad\qquad\quad CH_2 \\ HC\text{-----}CO \end{array}$$

(XXVI.)

$$CO_2H\cdot CO\cdot CMe_2\cdot CH_2\cdot COMe$$
(XXVII)
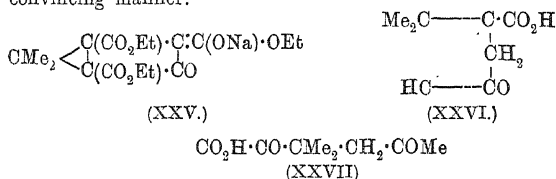
It is pointed out that the valencies in the *dicyclo*pentane system, especially the central connecting linking, are from theoretical considerations in a state of considerable strain, and far more so than in the *cyclo*propane ring of carone. Thus, although carone may be readily oxidised by potassium permanganate, with the formation of *trans*-caronic acid, it by no means follows that, under the influence of the same reagent, the *cyclo*propane ring in the substances under discussion ought to be expected to behave in a similar fashion and to remain intact. As a matter of fact, this is not the case, and the ring is broken by potassium permanganate, with the formation of open-chain acids. When, however, the acid XXVIII, which is the initial product of the hydrolysis of XXV, is oxidised by means of potassium ferricyanide and potassium carbonate, it gives rise to *trans*-caronic acid. The formation of

$$CMe_2\diagdown \begin{array}{l} CO\cdot CO_2H \\ CH_2\cdot CO\cdot CH_3 \end{array} \longrightarrow CMe_2\diagdown \begin{array}{l} C(OH)(CO_2H)\cdot CH_2 \\ CH_2\text{-----------}CO \end{array}$$

$$\downarrow$$

$$CMe_2\diagdown \begin{array}{l} C(CO_2H)\cdot CH_2 \\ CH\text{-----}CO \end{array}$$
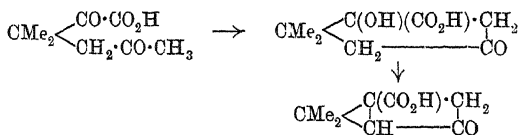
[73] W. H. Perkin, J. F. Thorpe, and C. Walker, *T.*, 1901, **79**, 729.
[74] N. J. Toivonen, *Annalen*, 1919, **419**, 176; *A.*, i, 49.
[75] E. H. Farmer and C. K. Ingold, *T.*, 1920, **117**, 1362.

XXVI from XXVII is therefore to be explained according to the above scheme (p. 90), the necessity for which is instructive. There is an obvious alternative scheme, in which the *cyclo*propane ring would be the first to be formed.

On account of its formulation by some chemists as an intermediate stage in the Wagner transformation, the hydrocarbon tricyclene (XXIX) has a special interest, and it has now been prepared[76] by a series of processes from tricyclenic acid (XXX), the constitution of which is not disputed.

$$CMe_2 < \begin{matrix} C(CO_2H) \cdot CH \cdot CO_2H \\ CH \text{———} CO \end{matrix}$$

(XXVIII.)

$$\begin{matrix} H_2C \text{———} CH \text{———} CH_2 \\ | \quad CMe_2 \quad | \\ HC \text{———} | \text{———} CH \\ \backslash \quad | \quad / \\ C \cdot CH_3 \end{matrix}$$

(XXIX.)

$$\begin{matrix} H_2C \text{———} CH \text{———} CH_2 \\ | \quad CMe_2 \quad | \\ HC \text{———} | \text{———} CH \\ \backslash \quad | \quad / \\ C \cdot CO_2H \end{matrix}$$

(XXX.)
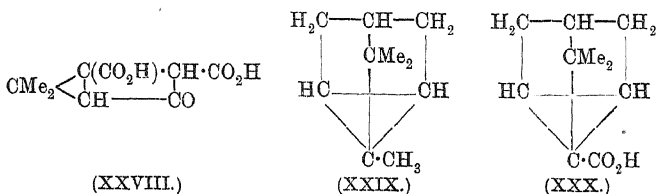
The methyl tricyclenate is reduced by sodium and alcohol to the corresponding primary alcohol, which is oxidised to an aldehyde, the hydrazone of which yields the desired hydrocarbon on heating at 180—195° with an alcoholic solution of sodium ethoxide. Tricyclene (m. p. 64—65°) is a relatively stable substance, which may be oxidised by potassium permanganate in acetic acid solution, with the formation of tricyclenic acid as one of the products, thus showing that the above process has not disturbed the ring system. It is converted by heating with sodium hydrogen sulphate into camphene, but the same change cannot be effected by means of zinc chloride in boiling benzene. The hydrocarbon might therefore be intermediate in the transformation of borneol, but not of *iso*borneol, into camphene. All arguments of this type are open to the objection that the abnormal energy conditions at the moment of reaction are not sufficiently taken into account.

Homocamphor (XXXI) has been prepared[77] by ring closure of hydrocamphorylacetic acid (XXXII), itself prepared by distillation of the malonic acid derivative produced in the electrolytic reduction of the condensation product of camphoric anhydride and diethyl sodiomalonate.

$$\begin{matrix} CH_2 \text{———} CH \text{———} CH_2 \\ | \quad CMe_2 \quad CH_2 \\ CH_2 \text{———} CMe \text{———} CO \end{matrix}$$

(XXXI.)

$$\begin{matrix} CH_2 \text{———} CH \cdot CH_2 \cdot CH_2 \cdot CO_2H \\ | \quad CMe_2 \\ CH_2 \text{———} CMe \cdot CO_2H \end{matrix}$$

(XXXII.)
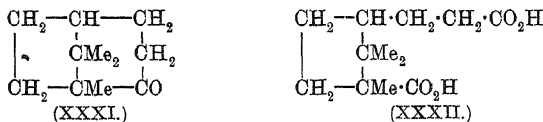
[76] P. Lipp. *Ber.*, 1920, **53**, [B], 769 ; *A*., i, 491.
[77] A. Lapworth and F. A. Royle, *T.*, 1920, **117**, 743.

The new substance is very like camphor in chemical and physical properties, and yields a similar series of derivatives. Its *iso*nitroso-derivative undergoes the Beckmann change, with the formation of a substance which yields homocamphoric acid on hydrolysis. This confirms the constitutions assigned to hydrocamphorylacetic acid and homocamphor.

Polycyclic Aromatic Groups.

Hydrindene Group.—Ethyl ββ-diphenyl-lactate, in contradistinction from the acid itself, dissolves in concentrated sulphuric acid to a green solution, from which 3-phenylindone (XXXIII) and two isomeric diphenyltruxones can be isolated.[78] The diphenyltruxones are colourless dimerides of the orange-red phenylindone, and it is interesting to note that only one of them can be reduced to a tetrahydro-derivative, probably containing two ·CH·OH

(XXXIII.)   (XXXIV.)

groups, by means of hydrogen in the presence of palladium. The brown hydrocarbon, which is prepared by the dehydration of the product of the action of magnesium phenyl bromide on diphensuccindandione (9:12), can be oxidised by chromic acid in cold acetic acid solution, with formation of 2:2'-dibenzoylbenzil, $C_6H_4Bz·CO·CO·C_6H_4Bz$, and has therefore the constitution XXXIV.[79]

A series of similar substances has been prepared and investigated.

Naphthalene Group.—Chlorinated nitronaphthalenes not readily obtained in other ways may be prepared by the nitration of the naphthalene chlorides followed by removal of the elements of hydrogen chloride. Thus naphthalene tetrachloride and nitric acid yield a resinous nitro-derivative, which is transformed by weak alkaline reagents into 5:8-dichloro-1-nitronaphthalene.[80] An extended study[81] of the reduction of α-naphthylamine shows that, in the presence of a neutral solvent, sodium and ethyl, butyl or amyl alcohols lead to the production of 5:8-dihydro-1-naphthylamine. This is also the product when ethyl or butyl alcohol is

[78] Remo de Fazi, *Gazzetta*, 1919, **49**, ii, 253; *A.*, i, 316.
[79] K. Brand and H. Ludwig, *Ber.*, 1920, **53**, [B], 809; *A.*, i, 486.
[80] O. Matter, *D.R.-P.* 317755; *A.*, i, 429.
[81] F. M. Rowe, *J. Soc. Chem. Ind.*, 1920, **39**, 241; *A.*, i, 609.

employed alone, but with amyl alcohol the reaction proceeds further, and *ar*-tetrahydro-α-naphthylamine is obtained. The explanation is that only under suitable conditions of temperature and alkyl-oxide concentration does the above-mentioned dihydro-derivative undergo isomerisation to 7:8-dihydro-1-naphthylamine, and that this isomerisation is an essential preliminary of reduction to the tetrahydro-stage. Similar results were obtained with naphthalene itself, which is first reduced to 1:4-dihydronaphthalene, isomerised to 1:2-dihydronaphthalene, and only then further reduced to tetrahydronaphthalene. In the catalytic reduction of naphthalene and α-naphthylamine dissolved in various solvents and in pre-sence of nickel, it was found that the reduction almost always stopped at the first stage mentioned above.

Anthracene Group.—Phenols may be condensed with phthalic anhydride and its substitution products in the presence of aluminium chloride, and good yields are obtained when the solvent is *s*-tetrachloroethane.[82] The carboxybenzoyl group is intro-duced in the ortho-position to the phenolic hydroxyl, and in many cases the benzoylbenzoic acids formed can be smoothly dehydrated to anthraquinones. For example, 4-chloro-1-hydroxyanthra-quinone can be prepared in this way from phthalic anhydride and *p*-chlorophenol.[83] In the section (see above) in which brief mention is made of the work of Dimroth on carminic acid, it was noted that two of the hydroxyl groups can be acetylated only with difficulty. This is a general property of hydroxyl groups in the α-positions in the anthraquinone nucleus. 1-Hydroxyanthra-quinone is scarcely attacked under the conditions which suffice to complete the acetylation of the 2-derivative, and purpurin and alizarin-bordeaux can be readily changed to mono-2-acetates.[84]

When the hydrochloride of 1-aminoanthraquinone is ex-haustively chlorinated in acetic acid solution, it yields the com-pound XXXV, which may be reduced by stannous chloride in acetic acid to 2:4-dichloro-1-hydroxyanthraquinone, or by ammonium chloride in acetic acid to 2:3:4-trichloro-1-hydroxy-anthraquinone. The pentachloro-derivative is hydrolysed by warm sulphuric acid to tetrachlorohydroxybenzoylbenzoic acid (XXXVI), and at a higher temperature to phthalic acid and 2:3:4:5-tetra-chlorophenol.[85]

Methyleneanthraquinone (XXXVII), a stable, pale yellow, crystal-

[82] F. Ullmann and W. Schmidt, *Ber.*, 1919, **52**, [B], 2098; *A.*, i, 53.

[83] F. Ullmann and A. Conzetti, *ibid.*, 1920, **53**, [B], 826; *A.*, i, 488.

[84] O. Dimroth, O. Friedemann, and H. Kammerer, *ibid.*, 481; *A.*, i, 443.

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[85] K. Fries and E. Auffenberg, *ibid.*, 23; *A.*, i, 236.

lme substance, is obtained by the condensation of a cold alkaline solution of anthranol with an excess of formaldehyde.[86]

$$C_6H_4 \underset{CO\cdot\underset{|}{C}\cdot CCl_2\cdot CHCl}{\overset{CO\cdot\underset{|}{C}\cdot CO-CCl_2}{<}}$$

(XXXV.)

$$CO_2H\cdot C_6H_4\cdot CO \underset{Cl}{\overset{OH}{<}} \underset{Cl}{\overset{Cl}{>}}$$

(XXXVI.)

$$C_6H_4 \underset{C(:CH_2)}{\overset{-CO-}{<}} > C_6H_4$$

(XXXVII.)
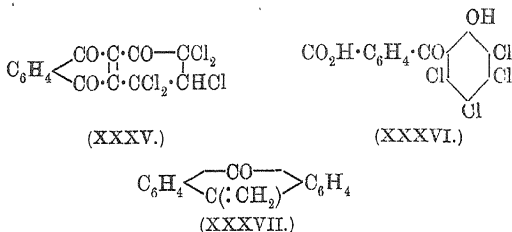
Polynuclear Groups.—Benzanthrone and most of its derivatives which have been examined in this connexion readily yield crystalline oxonium salts.[87]   The ferrichlorides may be isolated from an acetic acid solution containing ferric chloride, but the salts do not separate in the presence of excess of hydrochloric acid. Indeed, it is necessary to avoid the addition of the latter acid, sufficient of which for the formation of the double salt is derived from the hydrolysis of a portion of the ferric chloride.   A dihydroxy-benzanthrone obtained by condensation of deoxyalizarin and glycerol in the presence of sulphuric acid is found to be readily methylated, and is regarded as having the constitution XXXVIII. Since the substance, which is termed "benzalizarin," has dyeing properties on mordants which closely resemble those of alizarin itself, it becomes clear that the propinquity of the two hydroxyl groups of the latter substance to the carbonyl of the quinone nucleus is not so important a factor as has been imagined, and *p*-quinonoid formulæ are suggested for the lakes of alizarin and benzalizarin.

(XXXVIII.)
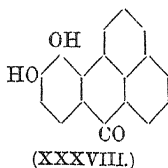
Perylene may be conveniently obtained in good yield by heating 2:2′-dihydroxy-1:1′-dinaphthyl at 400—500° with a halogen compound of phosphorus and phosphorous acid.[88]   This hydrocarbon is 1:8-dinaphthylene, and the reaction is evidently one involving rearrangement, but this is not surprising under the conditions.

[86] K. H. Meyer, *Annalen*, 1920, **420**, 134; *A.*, i, 747.
[87] A. G. Perkin, *T.*, 1920, **117**, 696.
[88] F. Hansgirg and A. Zinke, *Monatsh.*, 1919, **40**, 403; *A.*, i, 541.

Compounds containing Boron, Phosphorus, and Metals.

A communication on boranilide has appeared[89] which is crowded with astonishing statements, but it is necessary to point out that the experiments as described hardly bear the construction which is put on them, and the analytical data supplied are quite inadequate to support even the views on the composition of the substances which have been prepared.

The action of aliphatic diazo-compounds on tertiary phosphines leads to the production of a new class of phosphorus derivatives termed phosphazines. The reaction is an additive one proceeding in accordance with the scheme:

$$CR_2 \colon N \colon N + PR_3 \longrightarrow R_2 C \colon N \cdot N \colon PR_3.$$
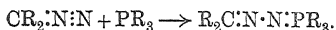
The products are basic, although this property is less developed when arylphosphines are the starting points. Triphenylphosphine-benzophenoneazine, $PPh_3 \colon N \cdot N \colon CPh_2$, is obtained from triphenylphosphine and diphenyldiazomethane. It is slowly hydrolysed to benzophenonehydrazone and triphenylphosphine oxide. On being heated in a vacuum it loses nitrogen, and is converted into triphenylphosphinediphenylmethylene, $PPh_3 \colon CPh_2$, which crystallises in red leaflets. When azides are added to phosphines the phosphazines which may be assumed to be formed initially decompose spontaneously, with the production of still another new type—the phosphineimines. Thus phenylazoimide and triphenylphosphine yield triphenylphosphinephenylimine, $PPh_3 \colon NPh$, when mixed in dry ether. This imine reacts with diphenylketen in benzene solution in accordance with the scheme:

$$PPh_3 \colon NPh + CPh_2 \colon CO = \begin{array}{c} PPh_3 \cdot NPh \\ | \qquad | \\ O \!-\!\!-\!\!-\! C \colon CPh_2 \end{array} \longrightarrow O \colon PPh_3 \text{ and } NPh \colon C \colon CPh_2$$
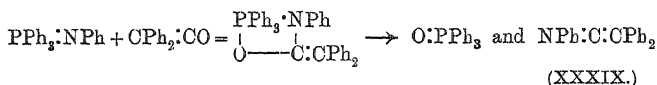
(XXXIX.)

The compound, XXXIX, is the first member of the series of the keten-imines.[90] An enormous number of aromatic arsenic derivatives have been prepared and described,[91] but few new methods have been elaborated. The introduction of mercury in aromatic compounds is another subject that has been much investigated, and it appears to be possible to effect substitutions by

[89] T. C. Chaudhuri, *T.*, 1920, **117**, 1081.

[90] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635; *A.*, i, 106; *Ber.*, 1920, **53**, [B], 72; *A.*, i, 228.

[91] R. G. Fargher, *T.*, 1920, **117**, 865; W. A. Jacobs and M. Heidelberger, *J. Amer. Chem. Soc.*, 1919, **41**, 1587, 1600, 1610, 1809, 1822, 1826, 1834; *A.*, i, 107—117; compare *Brit. Pat.* 128181.

means of mercuric acetate in substances which are not affected by reagents that might be regarded as much more powerful. Phenol ethers react even with aqueous mercuric acetate to yield additive compounds, which are instantly transformed by sodium chloride into products mercurated in the nucleus. At 50° p-tolyl methyl ether gives the substance $3C_6H_4Me \cdot OMe \cdot Hg(C_2H_3O_2)_2, 2HgO$, and by subsequent treatment with sodium chloride the substance

$$C_6H_3Me \cdot OMe \cdot HgCl.^{92}$$
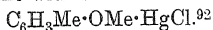
Mercuration differs from most substitution processes in that there is very little regularity, and each case has to be separately investigated. Lead tri-p-2-xylyl has been prepared[93] by the action of lead dichloride on the calculated amount of magnesium p-2-xylyl bromide, and this crystalline substance exhibits analogy to triphenylmethyl in its behaviour. It is bimolecular in benzene, and its solutions are coloured. At −40° it combines with bromine in pyridine to yield lead tri-p-2-xylyl bromide, whilst in chloroform at −10° the product is lead di-p-2-xylyl dibromide. Alkyl derivatives of bivalent tin have not yet been isolated in a pure condition, but the aryl derivatives, as usual, have proved more amenable and exhibit interesting properties.[94]   Tin diphenyl is obtained by the addition of finely powdered stannous chloride to an ethereal solution of magnesium phenyl bromide. It is bright yellow, and gives yellow solutions. When freshly prepared it has the normal molecular weight, but five-fold polymerisation soon occurs in benzene solution.   R. ROBINSON.

PART III.—HETEROCYCLIC DIVISION.

THE work now to be reviewed has not equalled that of pre-war years in volume, but the progress achieved in various directions, notably in connexion with the alkaloids, has been such as to merit a fairly detailed account. At the same time, one or two investigations, which have extended over some years, appear to have reached a point at which they may conveniently be dealt with as a whole. For these reasons, this Report will probably be found to be not much shorter than those which have preceded it.

Some Aspects of the Addition Theory of Reactions.

Although the addition theory of reactions is very widely accepted, there is probably divergence of opinion as to whether, for instance, the equation:

[92] W. Manchot and F. Bössenecker, *Annalen*, 1920, **421**, 331; *A.*, i, 780.
[93] E. Krause and M. Schmitz, *Ber.*, 1919, **52**, [B], 2165; *A.*, i, 197.
[94] E. Krause and R. Becker, *ibid.*, 1920, **53**, [B], 173; *A.*, i, 340.

$$\begin{array}{llll} X{\cdot}C & A & X{\cdot}C{\cdot}A & X{\cdot}C{\cdots}A & X{\cdot}C{\cdots}A-B \\ \parallel \ + \ | & | & | & | \\ Y{\cdot}C & B & X{\cdot}C{\cdot}B & Y{\cdot}C{\cdots}B & Y{\cdot}C{\cdots} \\ & & & \text{(I.)} & \text{(II.)} \end{array}$$
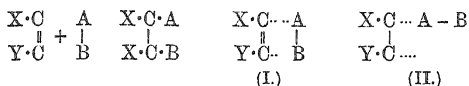
is an adequate expression of the process of saturation of a double bond. Thus Kekulé supposed that the final product was preceded by the double molecule (1), whilst more recently it has been assumed—and the view seems intrinsically more probable—that a still earlier stage is represented by (II). From this point of view much interest attaches to the direct formation of a cyclic structure by an additive reaction. With the exception of certain reactions of the ketens, all instances of this kind hitherto known depend on the union of similar molecules to form polymerides. Although these products are doubtless better represented by formulæ with ordinary rather than subsidiary linkages,[1] it seems more rational to consider them as the outcome, not of an instantaneous change, but of a continuous series of gradual changes, the phases of which are represented by (II) and (I). In the writer's view such a conception also supplies a simple explanation of the frequency with which four- rather than six-membered rings are produced in such cases. From the kinetic point of view, a reaction between two molecules is much more likely to occur than one between three, and similarly, unless other factors of an adverse kind operate, saturation of a preliminary product of the type (II) is more likely to occur by intramolecular rearrangement to type (I) than by intermolecular reaction with another molecule resulting in the formation of a six-membered ring. In illustration of this, a four-membered heterocyclic ring (IV) is produced with guaiacol when o-methoxyphenyl benzylidenehydrazinocarboxylate (III) is heated [2]:

$$CHPh{:}N{\cdot}NH{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}OMe \longrightarrow$$
$$\text{(III.)}$$

$$OH{\cdot}C_6H_4{\cdot}OMe + CHPh{:}N{\cdot}N{\cdot}CO \longrightarrow CHPh{:}N{\cdot}N{<}^{CO}_{CO}{>}N{\cdot}N{:}CHPh$$
$$\text{(IV.)} \qquad \downarrow$$

$$H_2N{\cdot}N{<}^{CO{\cdot}NH}_{CO{\cdot}NH} \longleftarrow CHPh{:}N{\cdot}N{<}^{CO{\cdot}NH}_{CO{\cdot}NH}$$
$$\text{(VI.)} \qquad\qquad \text{(V.)}$$

$$CHPh{:}N{\cdot}N{<}^{CO}_{CO}{>}N{\cdot}NH_2$$
$$\text{(VII.)}$$
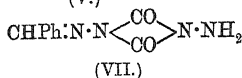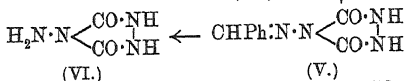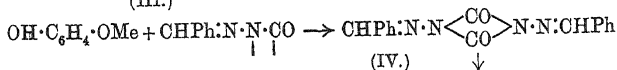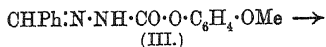
Although a trimeric formula supplies an equally good explanation of the successive formation of benzylideneurazine (V) and of

[1] H. Staudinger, Ber., 1920, 53, [B], 1073; A., i, 517.

[2] O. Diels and H. Grube, ibid., 854; A., i, 505; compare also the polymerisation of protoanemonin to anemonin, p. 114.

E

urazine itself (VI) on heating the compound with hydrochloric acid, the production of a compound corresponding in composition with the formula (VII) is only explicable on the basis of the dimeric formula.

That cyclic structures may also result from the combination of dissimilar molecules is evidenced by the formation of the acid chloride (I) with the corresponding anhydride (II) by the addition of phosphorus trichloride to phenyl styryl ketone in the presence of acetic anhydride [3]:

$$\begin{array}{c} \text{CPh:O} \\ \text{CH:CHPh} \end{array} \quad \begin{bmatrix} \text{CPh}\!-\!\!-\!\text{O} \\ \text{CH·CHPh} \end{bmatrix}\!\!>\!\!PCl_3 \end{bmatrix} \longrightarrow$$

$$\begin{array}{c} \text{CPh}\!-\!\!-\!\text{O} \\ \text{CH·CHPh} \end{array}\!\!>\!\!POCl \longrightarrow \left(\begin{array}{c} \text{CPh}\!-\!\!-\!\text{O} \\ \text{CH·CHPh} \end{array}\!\!>\!\!PO\right)$$

$$\text{(I.)} \qquad\qquad\qquad \text{(II.)}$$

The reaction is the first in which it has been found that two valencies of the same atom are utilised to satisfy the unsaturation of a second molecule. Perhaps still more remarkably, it has been shown [4] that the products of the action of phosphorus trichloride on aldehydes, which are decomposed by water to form hydroxyphosphonic acids,[5] are to be represented by formulæ of the type (III). In this case also a mixture of an acid chloride (IV) and an anhydride (V) is produced in the presence of acetic anhydride, those from benzaldehyde being represented by the formulæ (IV) and (V):

$$\begin{array}{c} \text{HPh·O} \\ \diagdown\!\diagup \\ \text{P}\,\text{l}_3 \end{array} \longrightarrow \begin{array}{c} \text{CHPh·O} \\ \diagdown\!\diagup \\ \text{POCl} \end{array} \qquad \begin{bmatrix} \text{CHPh O} \\ \diagdown\!\diagup \\ \text{PO} \end{bmatrix}_2\!\!O \longrightarrow$$

$$\text{(III.)} \qquad\quad \text{(IV.)} \qquad\qquad \text{(V.)}$$

$$\begin{array}{c} \text{CHPh·O} \\ \diagdown\!\diagup \\ \text{PO·OH} \end{array} \longrightarrow \begin{array}{c} \text{CHPh·OH} \\ \big| \\ \text{PO(OH)}_2 \end{array}$$

$$\text{(VI.)} \qquad\quad \text{(VII.)}$$

An unexpected point of difference between the two series of compounds is that in this case the free monobasic acid (VI) is sufficiently stable to be isolated. It reduces potassium permanganate slowly, whereas the hydroxyphosphonic acid (VII) suffers immediate oxidation.

In yet another instance, the formation of a cyclic structure has

[3] J. B. Conant and A. A. Cook, *J. Amer. Chem. Soc.*, 1920, **42**, 830; *A.*, i, 454.

[4] J. B. Conant and A. D. Macdonald, *ibid.*, 2337; *A.*, 1921, i, 69.

[5] W. Fossek, *Monatsh.*, 1884, **5**, 120, 627; 1886, **7**, 121; *A.*, 1884, 833; 1885, 504; 1886, 529.

been presumed. Thus, a mixture of two stereoisomeric forms of ethyl αβ-dinitrocinnamate is produced by the action of nitrogen peroxide on ethyl phenylpropiolate, but the first product of their interaction in light petroleum solution is a labile, crystalline compound of the two in equimolecular proportions.[6] This product decomposes into its components if the attempt be made to isolate it in the ordinary way, but, on the other hand, it gradually passes over in a closed vessel into ethyl phenylpropiolate and ethyl dinitrocinnamate. The reactions are expressed as follows:

$$2CPh\vdots C\cdot CO_2Et + 2NO_2 \longrightarrow \begin{matrix} CPh\equiv C\cdot CO_2Et \\ NO_2 \quad NO_2 \\ CPh\vdots C\cdot CO_2Et \end{matrix} \longrightarrow \begin{matrix} CPh\equiv C\cdot CO_2Et \\ NO_2 \quad NO_2 \\ + \\ CPh\vdots C\cdot CO_2Et \end{matrix}$$

although it must be observed that no evidence is supplied as to the molecular weight of the intermediate compound.

It has also been found necessary to apply ideas of the kind referred to above to certain reactions of benzoxazole.[7] The ordinary formula (I) for this compound represents it as an imino-ether, which on hydrolysis would be expected to give an o-acylhydroxyaniline, whilst an o-acylaminophenol is actually obtained. It cannot be assumed that the compound (II) is first produced, since compounds of this type revert to oxazoles when heated:

(I.)   (II.)

The change is therefore represented in the following manner:

[6] H. Wieland, *Ber.*, 1920, **53**, [B], 1343; *A.*, i, 737.
[7] S. Skraup, *Annalen*, 1919, **419**, 1; *A.*, 1919, i, 598.

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$$\begin{matrix} CPh{:}O \\ CH{:}CHPh \end{matrix} \rightarrow \left[\begin{matrix} CPh{---}O \\ CH{\cdot}CHPh \end{matrix} {>}PCl_3 \right] \rightarrow$$

$$\begin{matrix} CPh{---}O \\ CH{\cdot}CHPh \end{matrix} {>}POCl \rightarrow \left(\begin{matrix} CPh{---}O \\ CH{\cdot}CHPh \end{matrix} {>}PO \right)_2;$$

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$$\begin{matrix} CHPh{\cdot}O \\ \diagdown\diagup \\ P\cdot l_3 \end{matrix} \rightarrow \begin{matrix} CHPh{\cdot}O \\ \diagdown\diagup \\ POCl \end{matrix} \rightarrow \left[\begin{matrix} CHPh\ O \\ \diagdown\diagup \\ PO \end{matrix} \right]_2 O \rightarrow$$

$$(III.) \qquad (IV.) \qquad\qquad (V.)$$

$$\begin{matrix} CHPh{\cdot}O \\ \diagdown\diagup \\ PO{\cdot}OH \end{matrix} \rightarrow \begin{matrix} CHPh{\cdot}OH \\ PO(OH)_2 \end{matrix}$$

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although it must be observed that no evidence is supplied as to the molecular weight of the intermediate compound.

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[7] S. Skraup, *Annalen*, 1919, **419**, 1; *A.*, 1919, i, 598.

the decomposition of the intermediate product being attributed to the gradually increasing engagement of "valency lines" of the ring oxygen atom by one of the hydrogen atoms of the water molecule, and a consequent weakening of the cyclic structure. The velocity of hydrolysis is thus largely dependent on the rate of formation of the additive compound, which, in turn, varies with the amount of residual affinity available on the carbon atom after the requirements of the group R have been satisfied. The time required for 50 per cent. hydrolysis of various derivatives under standardised conditions is therefore considered to be some measure of the affinity of the group R. The following results were obtained:

R.	Time.	R.	Time.	R.	Time.
Benzyl	35 minutes	cycloHexyl	5 hours	Phenyl	74 hours
Methyl	40 ,,	isoButyl	5½ ,,	p-Tolyl	more
n-Hexyl	3 hours	tert. ..	7½ ,,	ι-Naphthyl	than
				p-Anisyl	120 hours

It will be seen that the order of these measurements is in general agreement with those which may be deduced from observations of various other reactions.[8]

In yet another direction the results of a long series of investigations[9] are summed up as showing "how many factors influence ring-formation and rupture, and how little present-day formulæ suffice to explain the contradictory behaviour of apparently similarly constituted compounds." Thus, contrary to what might be expected, 1 : 1-dialkylcoumaranones, as well as the non-alkylated compounds, are apparently more stable than 1-alkyl derivatives, which frequently suffer rupture of the five-membered ring and give disemicarbazones instead of the monosemicarbazones obtained in other cases:
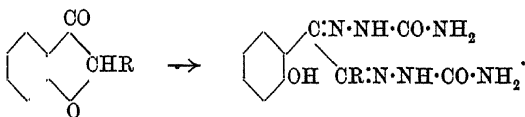
With p-nitrophenylhydrazine, however, coumaranones unsubstituted in the five-membered ring in general give osazones, this reac-

[8] Compare, for example, J. v. Braun, *Ber.*, 1904, **37**, 2812, 2915; 1907, **40**, 3914, 3933; 1909, **42**, 2532; *A.*, 1904, i, 731, 918; 1907, i, 899, 960; 1909, i, 604. H. Meerwein, *Annalen*, 1919, **419**, 121; *A.*, i, 2.

[9] K. von Auwers and others, *ibid.*, 1908, **41**, 4233; 1911, **44**, 3692; 1914, **47**, 2334, 2585, 3292; 1915, **48**, 85; 1917, **50**, 221, 1149; 1919, **52**, [B], 77, 92; 1920, **53**, [B], 428; *Annalen*, 1919, **418**, 69; 1920, **421**, 1; *A.*, 1909, i, 45; 1912, i. 107; 1914, i, 1136; 1915, i, 154, 440, 442; 1917, i, 277; 1918, i, 27; 1919, i, 217; 1920, i, 866.

tion serving to distinguish them from chromanones, which give hydrazones :
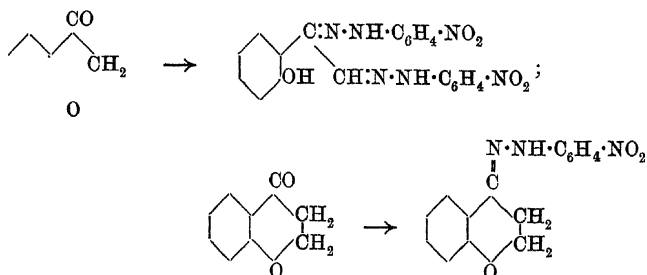
The only exception to this rule so far observed is 3 : 5-dimethyl-coumaranone, from which a hydrazone is obtained. The formation of 4-bromo-1 : 1 : 3 : 5-tetramethylcoumaranone as the sole product of the action of sodium hydroxide on α-bromo*iso*butyryl-4-bromo-*s*-xylenol is similarly in contrast with the production of 2 : 5-dimethyl-chromanone from α-bromo*iso*butyryl-*p*-cresol :
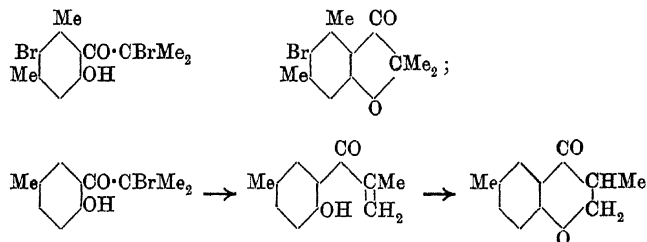
Whilst this exceptional behaviour on the part of *s*-xylenol derivatives recalls that observed in experiments on coupling [10] and in Friedel-Crafts syntheses,[11] and may be due to differences in the distribution of affinity, the experimental material at present available is insufficient to warrant the final adoption of this view.

Unsaturated compounds of the type indicated as an intermediate stage in the last of the above reactions form chromanones under the catalytic influence of alkali, as do their dibromides when alkali is employed to remove hydrogen bromide. On the other hand,

[10] K. von Auwers and F. Michaelis, *Ber.*, 1914, **47**, 1275; K. von Auwers and E. Borsche, *Ber.*, 1915, **48**, 1716; *A.*, 1914, i, 744; 1916, i, 85.

[11] K. von Auwers and E. Borsche, *ibid.*, 1915, **48**, 1698; *A.*, 1916, i, 34.

coumarans are obtained from o-allylphenols and coumarones from the dibromides of their acetates by treatment with alkali [12]:
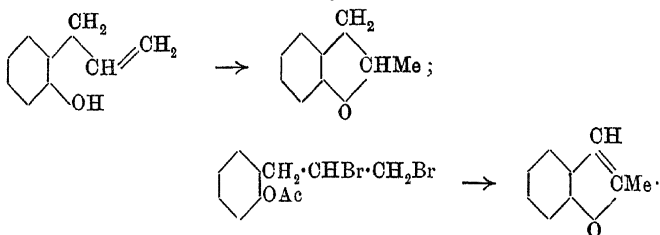
In explanation of this, it is suggested that the spatial configurations of the unsaturated side-chains in the two pairs of compounds differ, and are as represented in the formulæ.

Another notable reaction is that of 5-hydroxycoumarone-4-aldehyde, which is prepared from 5-hydroxy-2-methylcoumarone by the action of hydrocyanic acid in the presence of hydrogen chloride.[13] This compound, by condensation with acetic anhydride and sodium acetate, gives the corresponding acrylic acid:
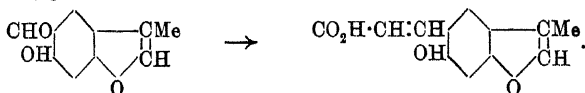
and all attempts to produce a coumarin from it by internal condensation failed. The result is attributed to steric hindrance, but supporters of the Kekulé formula for benzene will probably prefer to look upon it as evidence, confirming that of Marckwald adduced many years ago, of a difference in the mode of linking of the pairs of carbon atoms in the benzene nucleus.

The Stability and Formation of Cyclic Compounds.

The relative stability of various saturated cyclic structures, containing a tertiary nitrogen atom, towards cyanogen bromide and of their quaternary methylammonium hydroxides (Hofmann's degradation) has been carefully studied in recent years.[14] As a result it was found that the series tetrahydro*iso*quinoline, 1-methylmorpholine, dihydro*iso*indole, pyrrolidine, piperidine, and tetra-

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[12] L Claisen, *Anna'en*, 1919, **418**, 84; *Ber.*, 1920, **53**,, [B], 322; *A.*, 1919, i, 266; 1920, i, 325; compare R. Adams and R. E. Rindfusz, *J. Amer. Chem. Soc.*, 1919, **41**, 648; *A.*, 1919, i, 340.

[13] P. Karrer, A. Glattfelder, and F. Widmer, *Helv. Chim. Acta*, 1920, **3**, 541; *A.*, i, 627.

[14] J. von Braun, *Ber.*, 1909, **42**, 2035, 2532; 1911, **44**, 1252; 1916, **49**, 2629; 1918, **51**, 96, 255; *A.*, 1909, i, 604; 1911, i, 563; 1917, i, 168, 169; 1918, i, 185, 268.

hydroquinoline represented a gradual increase in stability for each reaction. Dihydroindole, however, one of the most reactive compounds towards cyanogen bromide, was the most resistent to the Hofmann reaction. The striking observation has now been made [15] that the nitrogen ring of the morphine molecule, which also contains the grouping ·C·C·N· attached by the first carbon atom to an aromatic nucleus, exhibits a similar divergence, but in the opposite direction. It is more stable in the first, and less stable in the second, reaction than any of the foregoing systems. Similar variations in the relative stabilities of a series of compounds towards different reagents have, of course, been observed in other directions. In considering them, it is perhaps well to remember that, in terms of the addition theory, the stabilities actually compared are rather those of the intermediate complexes, which are not necessarily in the order of those of the original compounds, and that differences may therefore well occur between the results obtained with different reagents. Furthermore, whilst the conclusions in respect of cyanogen bromide were obtained by comparative experiments on the separate compounds, a different method was followed in the case of the Hofmann reaction. For example, 1-o-vinylbenzylpiperidine was obtained by the distillation of " piperidyltetrahydro*iso*quinolinium hydroxide ":
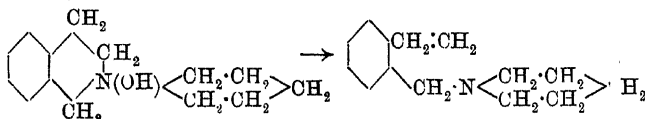
In this case, therefore, the piperidine is more stable than the tetrahydro*iso*quinoline ring, but a consideration of the results of the action of sodium amalgam on similar compounds [16] suggests doubts as to whether it is legitimate to extend this conclusion to pairs of compounds, one containing the piperidine ring, and the other the tetrahydro*iso*quinoline ring, and therefore as to whether a given ring structure in the various compounds containing it preserves precisely the same properties. Thus, from kairoline methochloride, kairoline (40 per cent.) and γ-phenylpropyldimethylamine (60 per cent.) are obtained:
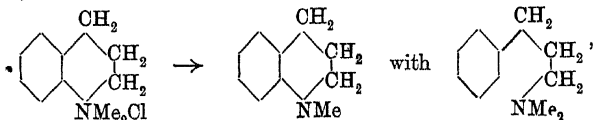
[15] *Idem*, *Ber.*, 1919, **52**, [B], 1999 ; *A.*, i, 79.

[16] J. v. Braun and others, *ibid.*, 1916, **49**, 501, 1283, 2613 ; 1917, **50**, 50 *A.*, 1916, i, 421, 742 ; 1917, i, 167, 282.

whilst N-methyldihydroindole (75 per cent.), β-phenylethyldimethyl-amine (8 per cent.), and o-ethyldimethylaniline (17 per cent.) are obtained from the methochloride of N-methyldihydroindole:
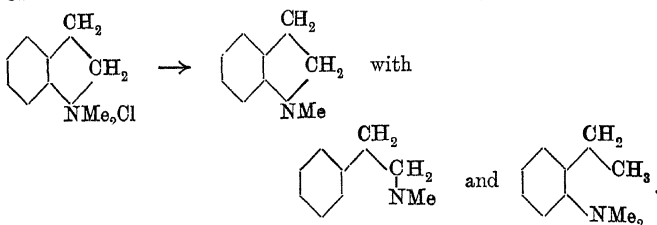
Yet lilolidine, prepared by boiling dihydroindole with 1-chloro-3-bromopropane, but not, be it noted, from tetrahydroquinoline and ethylene dibromide,[17] is not broken down by reduction of its methochloride. From 2-methyl-lilolidine the original base is recovered with a 10 per cent. yield of 1 : 2-dimethyl-7-n-propyldi-hydroindole[18]:
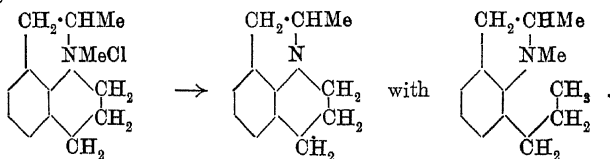
Cyclic Structures of New Types.

Results interesting in another respect have been obtained by the reduction of julolidine methochloride, from which the original base (63 per cent.) and the compound (I) (37 per cent.) are obtained[19]:

(I.)   (II.)
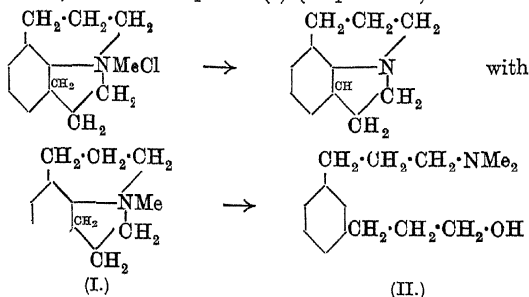
[17] E. Bamberger and H. Sternitzki, *Ber.*, 1893, **26**, 1291; *A.*, 1893, i, 520.

[18] J. v. Braun, K. Heider, and W. Wyczatkowska, *ibid.*, 1918, **51**, 1215; *A.*, 1919, i. 40.

[19] J. v. Braun and L. Neumann, *ibid.*, 1919, **52**, [B], 2015; *A.*, i, 87.

The constitution of the new base follows from its oxidation to *iso*-phthalic acid, and its degradation by the Hofmann reaction to a non-aromatic tertiary base (II), containing a non-phenolic hydroxyl group. Although the compound is unique in containing a ring structure attached to the benzene nucleus in the meta-position, very similar ten-membered rings attached in the ortho-position to benzene nuclei are contained in the products of the Hofmann reaction from tetrahydroberberine alkyl hydroxides,[20] and in crypto-pine and certain of its derivatives (compare p. 123).[21] It seems worthy of comment that all the products of this type hitherto obtained in the laboratory are produced, not synthetically, but by the breaking down of two simpler adjoining structures, and the easy conversion of the ten-membered ring of cryptopine into the two six-membered rings of *iso*cryptopine chloride suggests that in such ten-membered rings the carbon chain may preserve the con-figuration of the two rings from which it is derived. In spite, therefore, of the existence of the compounds in question, there is still room for doubt as to whether their synthesis, properly speaking, is possible.

A four-membered heterocyclic system of a new type appears to be present in the product of the action of nitrous acid on camphor-oxalic acid.[22] A transient blue colour suggests that the normal nitroso-compound (I) is first produced, but it gives place to a mono-basic acid, apparently according to the equation

$$C_{12}H_{15}O_5N + H_2O = C_{11}H_{17}O_4N + CO_2.$$
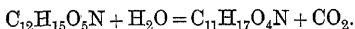
This acid gives a red coloration with ferric chloride, and hence contains an enolic grouping which, further, undergoes methylation before the carboxyl group. Although the acid is merely converted into what is probably a stereoisomeride by boiling concentrated potassium hydroxide solution, its dimethyl derivative is easily decomposed into ammonia and α-ketohomocamphoric acid (II). Further, the acid contains the complex $>N \cdot O \cdot$ as part of a ring, since it is easily reduced by ferrous hydroxide to camphidone-carboxylic acid (III). Although the nature of the changes

$$C_8H_{14} \Big\langle \substack{C(NO) \cdot CO \cdot CO_2H \\ CO}$$

(I.)

$$C_8H_{14} \Big\langle \substack{CO \cdot CO_2H \\ CO_2H}$$

(II.)

$$C_8H_{14} \Big\langle \substack{CH(CO_2H) \\ CO} \Big\rangle NH$$

(III.)
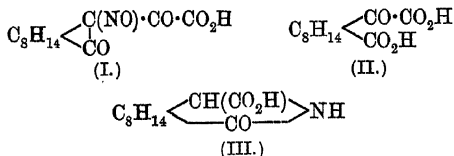
[20] F. L. Pyman, *T.*, 1913, **103**, 817.
[21] W. H. Perkin, *ibid.*, 1916, **109**, 815; 1919, **115**, 713.
[22] P. Chorley and A. Lapworth, *ibid.*, 1920, **117**, 728.

E*

involved remains obscure, it is concluded that the original product contains the skeleton (IV), and of the alternatives which meet this condition, preference is given to that represented by (V).

(IV.)   (V.)
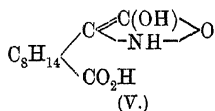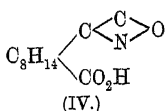
A Radicle containing Quadrivalent Nitrogen.

Dimethyl- and diethyl-tetrahydropyridyls[23] give yellowish-brown solutions in alcohol, which, especially in the presence of a little water or on warming, gradually become blue. In this condition they immediately absorb oxygen, with the formation of N-alkyl-pyridinium hydroxides, and give N-alkylpyridinium iodides with iodine.[24]   The coloured solutions further resemble those of tri-phenylmethyl in their diminished colour intensity at lower temperatures. Although no molecular weight determinations are quoted, it is concluded that dissociation occurs, and that the coloured solute is a radicle containing quadrivalent nitrogen rather than tervalent carbon:
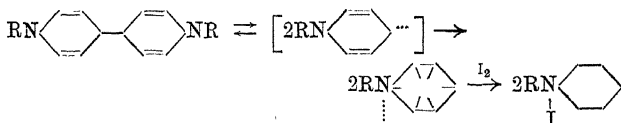
The latter may possibly be present in the yellow, ethereal solution or the pale green chloroform solution, since these give a yellow, amorphous product with iodine.

The dissociation is ascribed to the weakening effect of the various double bonds on the valencies of the γ-carbon atoms, but there is no discussion of the meaning, or the nature, of the change from tervalent carbon to quadrivalent nitrogen.

Stereoisomerism of Tervalent Nitrogen Compounds.

Well-defined stereoisomerism of tervalent nitrogen compounds has hitherto been observed only in the case of compounds, such as oximes, in which, according to the usual formulæ, the directions of two valencies are fixed by a double bond, and reference will be

[23] A. W. Hofmann, *Ber.*, 1881, 14, 1503; *A.*, 1881, 921; compare B. Emmert, *Ber.*, 1909, 42, 1997; 1917, 50, 31; 1919, 52, [B], 1351; *A.*, 1909, i, 602; 1917, i, 221; 1919, i, 455.
[24] B. Emmert, *ibid.*, 1920, 53, [B], 370; *A.*, i, 331.

made later to the first case of such isomerism observed among the hydrazones. A number of cases have, however, now been observed in which the directions of the two valencies are defined by participation of the nitrogen atom in a cyclic structure.

A closer examination of the isomerism of methyl*iso*pelletierine (I) and *dl*-methylconhydrinone (II), referred to in last year's Report, has confirmed it, and led to the discovery of further examples.[25] *iso*Pelletierine (III), which occurs naturally, and can also be obtained by the demethylation of methyl*iso*pelletierine, on re-methylation gives methyl*iso*pelletierine alone, thus differing from *dl*-conhydrinone (IV), which gives both this compound and *dl*-methylconhydrinone. Further, whilst *iso*pelletierine is recovered from its carboxylic ester (V) on alkaline hydrolysis, the corresponding derivative of *dl*-conhydrinone (VI) undergoes a remarkable reaction, which may have a significance in connexion with the processes of plant life, α-2-pyrrolidylbutan-β-one (VII) being produced in excellent yield. It is seen that these results are

$$
\begin{array}{cccc}
CH_2 & CH_2 & CH_2 & CH_2 \\
CH_2\ CH_2 & CH_2\ CH_2 & CH_2\ CH_2 & CH_2\ CH_2 \\
CH_2\ CH\cdot CH_2Et & CH_2\ CH\cdot COEt & CH_2\ CH\cdot COEt & CH_2\ CH\cdot COEt \\
NMe & NMe & NH & N\cdot CO_2Et \\
& (II.) & (IV.) & (VI.)
\end{array}
$$

$$
\begin{array}{cccc}
CH_2 & CH_2 & CH_2 & \\
CH_2\ CH_2 & CH_2\ CH_2 & CH_2\ CH_2 & CH_2\cdot CH_2 \\
CH_2\ CH\cdot COEt & CH_2\ CH\cdot COEt & CH_2\ CH\cdot COEt & CH_2\ CH\cdot CH_2\cdot COEt \\
MeN & HN & CO_2Et\cdot N & NH \\
(I.) & (III.) & (V.) & (VII.)
\end{array}
$$
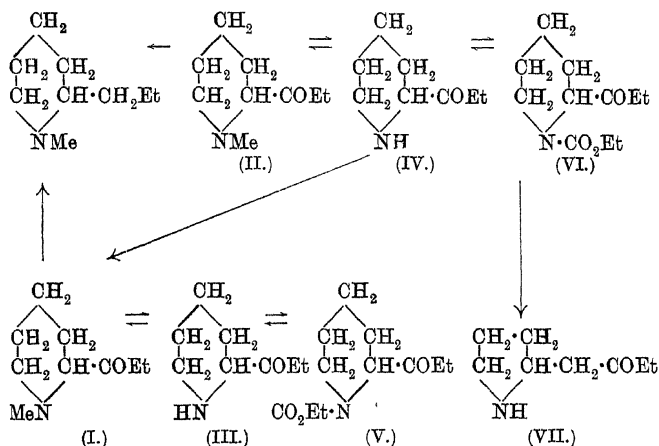
explicable on the basis of the configurations indicated, and originally assigned to the first pair of isomerides, on the ground of the failure through steric hindrance of *dl*-methylconhydrinone to react with semicarbazide, and its slower reaction with hydroxylamine and hydrazine. The isomerism in question is preserved when methyl *iso*pelletierine and *dl*-methylconhydrinone are reduced to the corresponding amino-alcohols, a distinct pair of products being obtained from each. The ketonic group is there-

[25] K. Hess, *Ber.*, 1919, **52**, [B], 1622; 1920, **53**, [B], 129; *A.*, i, 86, 329.

fore not essential to the isomerism, but the formation of the same
dl-methylconiine from both series suggests that the oxygen atom
may be in the present instance. This, however, is apparently not
always so, because the isomeric forms of 1-methyl-2-propyl(or *iso*-
butyl or benzyl)-tetrahydroquinoline [26] resemble the above com-
pounds in giving different quaternary ammonium salts, and are
probably examples of the same type of isomerism.

The considerable difference in properties exhibited by the
various pairs of isomerides is in marked contrast to the close agree-
ment between coniine and *iso*coniine. This, in conjunction with
the production of the same methylconiine from the above
isomerides, suggests doubts as to the reality of their isomerism,
and a careful investigation [27] has now shown that *iso*coniine is
merely a slightly impure form of coniine.

A whole series of stereoisomerides has been discovered among
the 2-acidyl derivatives of indazole.[28] Stable compounds are
obtained by the action of acetic, propionic, or benzoic anhydrides
on indazole, or its derivatives containing substituents in the
benzene nucleus. From acid chlorides, however, and either the
parent substances in presence of pyridine or their silver salts alone,
labile isomerides are produced which more or less readily pass
over into the stable forms. The inherent improbability of such
a formula as (I) excludes an explanation based on structural
isomerism, whilst the recovery of each from its double compounds
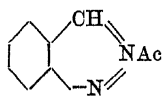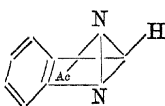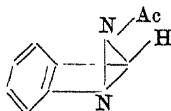
(I.)   (II.)   (III.)
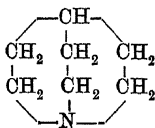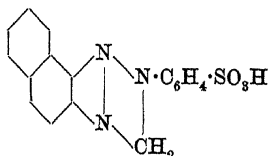
(IV.)   (V.)

with, for example, mercuric chloride shows that these are not
cases of physical isomerism. It is therefore suggested that the
relationship between them is represented by the formulæ (II) and

[26] M. Freund and E. Kessler, *J. pr. Chem.*, 1918, [ii], **98**, 233; *A.*, 1919,
i, 283.
[7] K. Hess and W. Weltzien, *Ber.*, 1920, **53**, [B], 139; *A.*, i, 330.
[28] K. von Auwers and M. Düesberg, *ibid.*, 1179; *A.*, i, 638.

(III). The analogy to the oximes suggested by these formulæ is strengthened by the fact that, as with acetophenoneoxime, so in the case of 2-acidyl derivatives of 3-methylindazole, only one form has been isolated. Pursuing this, the labile acidyl-indazoles are regarded as *syn-* (III) and the stable forms as *anti-*compounds (II).

In quinuclidine (IV), the three valencies of the nitrogen atom are fixed and directed towards the corners of a tetrahedron. The prediction is therefore made that it should be possible to obtain suitably chosen substitution derivatives in enantiomorphous forms, but experimental work in this direction has not got beyond the initial stages.[29] Its development will be awaited with interest, because the same conditions are present in 2-*p*-sulphophenyl-2 : 3-dihydro-1 : 2 : 4-naphtha*iso*triazine (V), the apparent resolution of which was reported some years ago.[30]

The optical activity of pelletierine and methyl*iso*pelletierine has been reaffirmed.[31]

Symmetric and Asymmetric Synthesis.

Consequent upon the elucidation of the structure of scopoline (p. 127), an interesting discussion[32] has developed as to the processes by which in plant life racemic mixtures, such as coniine, methylconiine, pelletierine, *iso*pelletierine, methyl*iso*pelletierine, atropine, laudanine, scopoline, paricine, cryptopine, arabine, cevadine, delphinine, and delphinidine, are sometimes produced. In the majority of these cases it is not unreasonable to assume that at some stage in their synthesis a process occurs independently of the plant organism, which is a symmetrical one. Thus *dl*-coniine (II) may possibly be produced by such a process from optically active conhydrin (I):

(I.)   (II.)
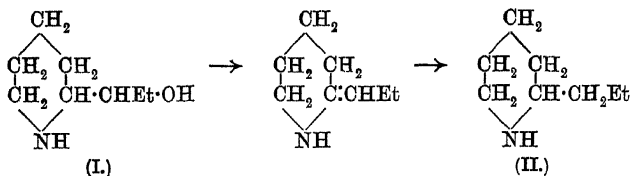
It seems, however, improbable that such a hypothesis can apply to the case of scopoline, because four asymmetric carbon atoms are

[29] J. Meisenheimer, *Annalen*, 1920, **420**, 190 ; *A.*, i, 761.

[30] T. S. Moore, *P.*, 1914, **30**, 182.

[31] G. Tanret, *Compt. rend.*, 1920, **170**, 1118 ; *A.*, i, 499.

[32] K. Hess and W. Weltzien, *Ber.*, 1920, **53**, [B], 119 ; H. Pringsheim, *ibid.*, 1375 ; K. Hess, *ibid.*, 1375 ; *A.*, i, 328, 774.

involved, and it would become necessary to assume that the majority of the stages of its formation are spontaneous processes. The conclusion therefore seems inevitable that the plant organism is capable of symmetric synthesis. Although cases of this kind are not entirely unknown in animal life, for example, the presence of dl-arabinose in urine as a result of certain disorders,[33] they are very exceptional. It appears, therefore, that the specific action of enzymes is considerably more pronounced in animal than in plant life.

Catechin.

The constitution of catechin has now been practically determined as a result of the study [34] of the methylated product of reduction of catechin tetramethyl ether,[35] which, on oxidation with alkaline permanganate, furnishes an acid, the molecule of which contains one atom of carbon less. Since this degradation is found to be common to compounds containing the ethyl group:

$$R \cdot CH_2 \cdot CH_3 \longrightarrow R \cdot CO_2H,$$
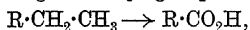
it would appear that the reduction product is $3:4:2':4':6'$-pentamethoxy-$\alpha\alpha$-diphenylpropane (A), which on oxidation would give $3:4:2':4':6'$-diphenylacetic acid (B), and these conclusions have been verified by synthesis. The acid was obtained from

(I.)   (A.)   (B.)
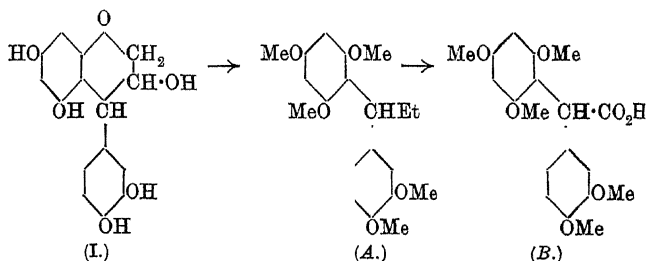
$3:4:2':4':6'$-pentamethoxydiphenylcarbinol through the corresponding chloride by means of the Grignard reaction. From its chloride and diazomethane, $3:4:2':4':6'$-pentamethoxydiphenylmethyl chloromethyl ketone is obtained, which by reduction is converted into the required propane derivative:

$$C_6H_2(OMe)_3 \cdot CH(OH) \cdot C_6H_3(OMe)_2 \longrightarrow$$
$$C_6H_2(OMe)_3 \cdot CH(CO_2H) \cdot C_6H_3(OMe)_2 \longrightarrow$$
$$C_6H_2(OMe)_3 \cdot CH(CO \cdot CH_2Cl) \cdot C_6H_3(OMe)_2 \longrightarrow$$
$$C_6H_2(OMe)_3 \cdot CHEt \cdot C_6H_3(OMe)_2.$$
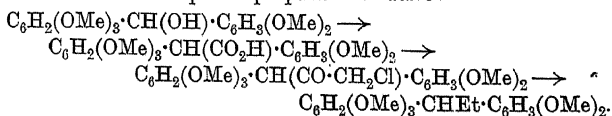
[33] Compare C. Neuberg, Ber., 1900, 33, 2243; 1902, 35, 1468; A., 1900, i, 539; 1902, ii, 417.   [34] M. Nierenstein, T., 1920, 117, 971, 1151.
[35] S. von Kostanecki and V. Lampe, Ber., 1907, 40, 720; A., 1907, i, 334.

The properties of each of these compounds are in accordance with anticipation, and the formula (I) is proposed for catechin, in place of the older formulæ (II) [36] and (III),[37] according to which the product referred to above would be either $2:4:6:3':4'$-pentamethoxy-3-ethyldiphenylmethane (IV) or $3:4:2':4':6'$-pentamethoxy-$\alpha\gamma$-diphenylpropane (V). Each of these compounds has been synthesised by the reduction of $2:4:6:3':4'$-pentamethoxy-3-ethylbenzophenone and $2:4:6$-trimethoxyphenyl $3:4$-dimethoxystyryl ketone respectively, and found to differ from the compound in

(II.) → (IV.)

(III.) → (V.)
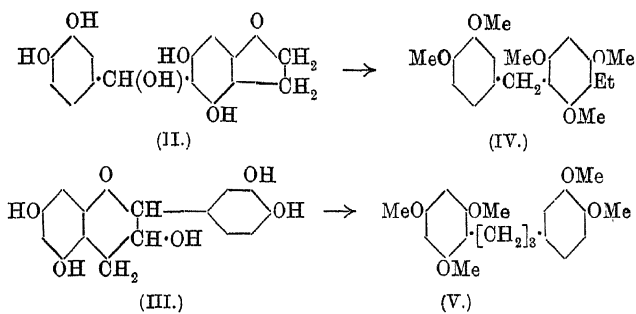
question. Finally, in confirmation of the new formula, reduction of 3-phenylchroman (VI) results in the formation of 2-hydroxy-$\alpha\alpha$-diphenylpropane (VII), from which 2-hydroxydiphenylacetic acid (VIII) is obtained on oxidation with potassium permanganate.

(VI.) → (VII.) → (VIII.)

(IX.) → (X.)
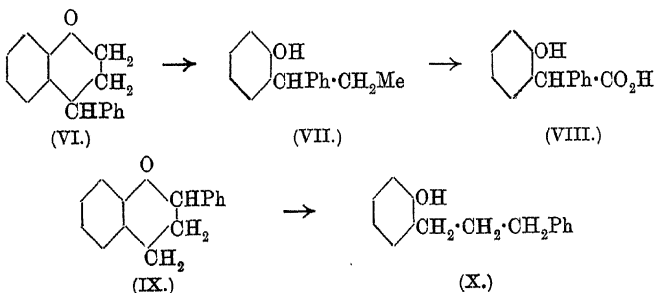
From 1-phenylchroman (IX), 2-hydroxy-$\alpha\gamma$-diphenylpropane (X) is obtained, and found to be stable towards permanganate.[38]

[36] S. von Kostanecki and V. Lampe, *Ber.*, 1907, **40**, 720; *A.,* 1907, i, 334.

[37] A. G. Perkin and E. Yoshitake, *T.*, 1902, **81**, 1172; compare H. Ryan and M. J. Walsh, *Sci. Proc. Roy. Dub. Soc.*, 1916, **15**, 113; *A.*, 1916, i, 722.

[38] (Miss) A. Greenwood and M. Nierenstein, *T.*, 1920, **117**, 1594.

The evidence is therefore so complete that it suffices merely to refer to another investigation,[38a] in which the identity is affirmed of the methylated reduction product with pentamethoxy-αγ-diphenyl-propane, although, remarkably enough, in other respects substantially the same account is given of the preparation and properties of this compound. In the circumstances, also, less interest attaches to experiments on the synthesis of compounds,[39] the structure of which is in close agreement with the formula (II). Thus, by the respective condensations of 5-hydroxy-2-methylcoumarone and 5-hydroxy-2-methylcoumaran with benzonitrile in the presence of hydrogen chloride, 5-hydroxy-2-methyldepsenone (I) and 5-hydroxy-2-methyldepsanone (II) are obtained, and from these by reduction the corresponding secondary alcohols:

(I.)

(II.)
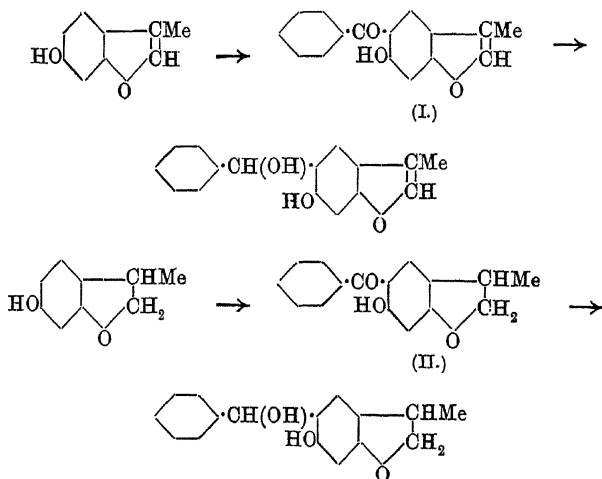
The Anthocyanins.

The evidence for the constitution of the anthocyanins, recorded some years ago,[40] was rounded off by a synthesis of pelargonidine described in a paper,[41] which, however, has only recently become available in this country. By condensation of 2:4:6-trihydroxy-

[38a] K. Freudenberg, *Ber.*, 1920, **53**, [B], 1416; *A.*, i, 752.

[39] P. Karrer and F. Widmer, *Helv. Chim. Acta*, 1919, **2**, 454; *A.*, 1919, i, 595.

[40] Compare *Ann. Reports*, 1914, **11**, 138; 1915, **12**, 156.

[41] R. Willstätter and L. Zechmeister, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, **34**, 886; *A.*, i, 561.

benzaldehyde with sodium methoxyacetate and the corresponding anhydride, 5 : 7-dimethoxyacetoxy-3-methoxycoumarin (I) is obtained. This compound, by successive treatment with sodium hydroxide and diazomethane, gives 3 : 5 : 7-trimethoxycoumarin (II), which reacts with magnesium p-anisyl bromide to form 3 : 5 : 7-trimethoxy-2-p-anisylpyrylium chloride (III), from which the methyl groups are removed by means of hydriodic acid. From the iodide thus produced a chloride (IV) is obtained, which is identical in every respect with that of natural pelargonidine [42]:
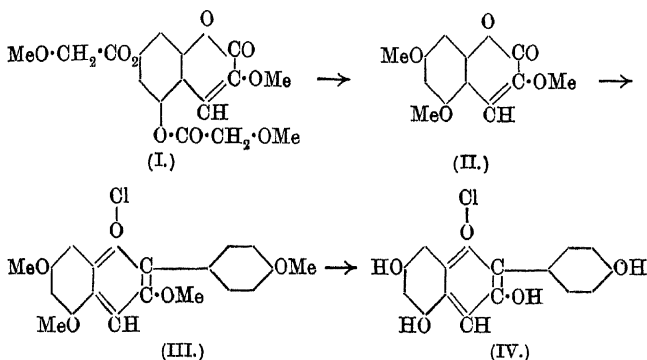
Some other Plant Products.

Anemonin (I), which is obtained with anemonic acid and proto-anemonin by the steam distillation of certain varieties of *Anemone* and *Ranunculus* [43] has now been shown to be an unsaturated lactone. It is a doubly unsaturated compound of the formula $C_{10}H_8O_4$, which exhibits the reactions of the carbonyl group,[44] yields oxalic and succinic acids on oxidation, and by acid or alkaline hydrolysis is converted into anemoninic acid (II). The last is an unsaturated compound, with reducing properties and existing in stereoisomeric forms, which gives γ-ketopimelic acid on oxidation. By catalytic reduction of anemonin,[45] a tetrahydro-derivative (III) and, finally, sebacic acid are produced, whilst a dihydro-derivative (IV) is produced in the presence of sodium amalgam, and this is converted by hydrolysis into anemonolic acid, which is found to be identical with dilævulic acid (V), and is obtained directly from anemonin by the

[42] R. Willstätter and E. K. Bolton, *Annalen*, 1915, **408**, 42 ; *A.*, 1915, i, 283.

[43] H. Beckurts, *Chem. Zentr.*, 1885, 776 ; *A.*, 1886, 365.

[44] *Ibid.*, *Arch. Pharm.*, 1892, **230**, 182 ; *A.*, 1892, 1241.

[45] Y. Asahina and A. Fujita, *J. Pharm. Soc. Japan*, 1919, 471 ; 1920, 1 ; 1920, No. 461 ; *A.*, i, 70, 493, 678.

action of cold hydriodic acid. The changes are represented by the following scheme:

$$CH_2 \cdot C \underset{O---CO}{\overset{CH{:}CH}{<}} \qquad CH_2 \cdot C \underset{O---CO}{\overset{CH \cdot CH_2}{<}} \qquad CH_2 \cdot C \underset{O---CO}{\overset{CH_2 \cdot CH_2}{<}}$$

$$CH_2 \cdot C \underset{O---CO}{\overset{CH{:}CH}{<}} \qquad CH_2 \cdot C \underset{O---CO}{\overset{CH \cdot CH_2}{<}} \qquad CH_2 \cdot C \underset{O---}{\overset{CH_2 \cdot CH}{<}}$$

$$\text{(I.)} \qquad\qquad\qquad \text{(IV.)} \qquad\qquad\qquad \text{(III.)} \quad \underset{\text{Sebacic}}{\downarrow}$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{acid}$$

$$\begin{array}{ll} CH_2 \cdot CO \cdot CH{:}CH \cdot CO_2H & CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H \\ CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H & CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H \\ \quad\text{(II.)} & \quad\text{(V.)} \end{array}$$
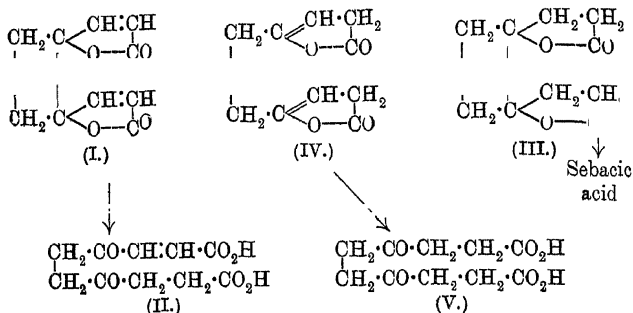
This interpretation is supported by the synthesis of protoanemonin (VI), a vesicant substance from which anemonin is derived by spontaneous polymerisation. Acetylation of β-bromolaevulic acid results in the formation of a lactone (VII), from which the elements of hydrogen bromide are removed by means of sodium acetate. The product, doubtless acetylacetoacrylic acid, on distillation furnishes protoanemonin:

$$CH_3 \cdot CO \cdot CHBr \cdot CH_2 \cdot CO_2H \quad \rightarrow \quad \underset{AcO}{\overset{CH_3}{>}}C \underset{O---CO}{\overset{CHBr \cdot CH_2}{<}} \quad \rightarrow$$

$$\left[\underset{AcO}{\overset{CH_3}{>}}C \underset{O---CO}{\overset{CH{:}CH}{<}} \right] \quad \rightarrow \quad CH_2{:}C \underset{O---CO}{\overset{CH{:}CH}{<}}$$

$$\text{(VII.)} \qquad\qquad\qquad\qquad\qquad\qquad \text{(VI.)}$$
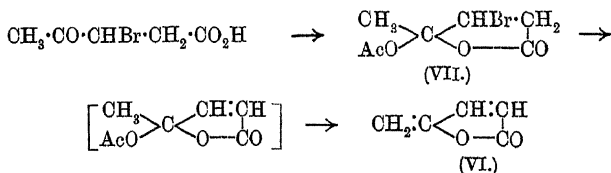
Anemonin has been similarly synthesised from dibromoangelica-lactone.

Hyptolide, another plant product, is also considered to be an unsaturated lactone, and is formulated as a derivative of dihydro-pyrone[46]:

$$\underset{CH \cdot CO \cdot O}{\overset{CH \cdot CMe_2}{>}}CMe \cdot [CH \cdot OAc]_3 \cdot CH_3.$$
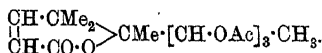
Elsholtzione, a ketone, $C_{10}H_{14}O_2$, obtained by steam distillation of *Elsholtzia cristata*,[47] yields *iso*valeric acid on oxidation, and by treatment with amyl nitrite and sodium ethoxide is degraded to 3-methylfuran-2-carboxylic acid (homopyromucic acid), a behaviour which is reproduced by the synthetic ketones obtained

[46] K. Gorter, *Bul. Jard. bot. Buitenzorg*, 1920, [iii], **1**, 327 ; *A*., i, 494.
[47] Y. Asahina and Y. Murayama, *Arch. Pharm.*, 1914, **252**, 435 ; *A*., 1915, i, 429.

by the action of magnesium alkyl haloids on pyromuconitrile. These reactions and the reduction of its hydrazone to 3-methyl-2-*iso*amylfuran (II) all point to the composition of the compound as being represented by the formula (I).[48]

$$
\begin{array}{ccc}
\underset{O}{\underset{\diagdown\diagup}{\overset{CH--CMe}{\underset{CH\quad C\cdot CO\cdot CH_2\cdot CHMe_2}{|\quad\quad|}}}} & \longrightarrow & \underset{O}{\underset{\diagdown\diagup}{\overset{CH--CMe}{\underset{CH\quad C\cdot C(:N\cdot NH_2)\cdot CH_2\cdot CHMe_2}{|\quad\quad|}}}} \longrightarrow
\end{array}
$$

(I.)

$$
\underset{O}{\underset{\diagdown\diagup}{\overset{CH--CMe}{\underset{CH\quad C\cdot CH_2\cdot CH_2\cdot CHMe_2}{|\quad\quad|}}}}
$$

(II.)
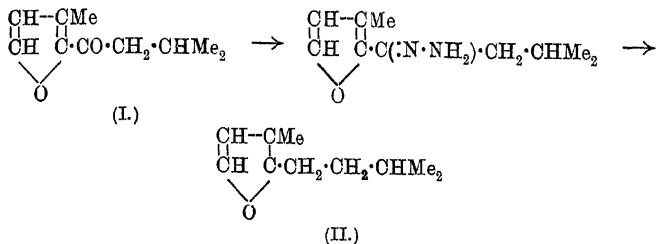
The Glyoxalines.

An investigation of the orientation of substitution derivatives of glyoxaline has given interesting results. Direct nitration,[49] and probably also direct sulphonation,[50] takes place in the 4-position. On reduction by cold stannous chloride solution, the 4-nitro-derivatives of 5- and 2-methylglyoxalines, and of glyoxaline itself, respectively give, not the amino-compounds (a small proportion in the case of the 5-methyl derivative being excepted), but α-alanine, α-amino-α-iminoethane, and glycine. The course of the changes in the last two cases is represented as follows : [51]

$$
(a)\quad \underset{NO_2\cdot C----N}{\overset{CH\cdot NH}{|}}\!\!>\!\!CMe \longrightarrow \left[\underset{NH_2\cdot C----N}{\overset{CH\cdot NH}{|}}\!\!>\!\!CMe\right] \longrightarrow
$$

$$
\left[\underset{CO----N}{\overset{CH_2\cdot NH}{|}}\!\!>\!\!CMe\right] \longrightarrow \underset{HN}{\overset{NH_2}{}}\!\!>\!\!CMe
$$

$$
(b)\quad \underset{NO_2\cdot C----N}{\overset{CH\cdot NH}{|}}\!\!>\!\!CH \longrightarrow \left[\underset{NH_2\cdot C----N}{\overset{CH\cdot NH}{|}}\!\!>\!\!CH\right] \longrightarrow
$$

$$
\left[\underset{CO----N}{\overset{CH_2\cdot NH}{|}}\!\!>\!\!CH\right] \longrightarrow \underset{CO_2H}{\overset{CH_2\cdot NH_2}{|}} .
$$
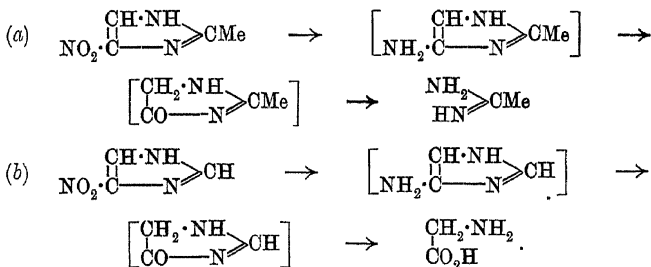
Although this is a plausible view of the reaction, it seems not very clear by what process the amino-compounds are converted into glyoxalones. The hypothesis, which may first suggest itself to the

[48] M. Asano, *J. Pharm. Soc. Japan*, 1919, 999 ; *A.*, i, 495.
[49] R. G. Fargher and F. L. Pyman, *T.*, 1919, **115**, 217.
[50] F. L. Pyman and L. A. Ravald, *ibid.*, 1920, **117**, 1429.
[51] R. G. Fargher, *ibid.*, 668.

reader and ascribe the change to a hydrolysis of the amino-deriv-
ative reacting in the imino-form, would probably not be accept-
able, because 4-amino-5-methylglyoxaline shows the reactions of a
true amine, whilst 2-aminoglyoxaline is a monoacidic, non-
diazotisable base, which does not give a benzylidene derivative.
It is therefore regarded as an imino-compound, although in this
case its stability towards acid may seem remarkable.

The Rhodanines.

The results of two investigations point to the existence of
tautomerism in the rhodanine series. Thus, whilst rhodanine
gives a colourless dibenzoyl derivative (I), a yellow monobenzoyl
derivative (II) is obtained from benzylidenerhodanine.[52] Further,

$$S \underset{CH=\!=\!C \cdot OBz}{\overset{C(SBz)\colon N}{<}} \qquad\qquad S \underset{C(\colon CHPh)\cdot CO}{\overset{C(SBz)=\!=\!N}{<}}$$

(I.) (II.)
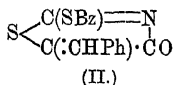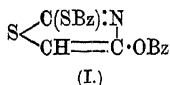
5-methyl-3-ethylrhodanine-5-acetic acid (III) is obtained in an
optically active form by the condensation of sodium l-methyl-
bromosuccinate with potassium ethyldithiocarbamate, but 3-phenyl-
5-methylrhodanine (IV), prepared from phenylthiocarbamide and
d-thiol-lactic acid, is inactive, owing to racemisation of the initial
product through its enolic form.[53]

$$S \underset{CMe(CH_2 \cdot CO_2H) \cdot CO}{\overset{CS\text{------------}NEt}{<}} \qquad\qquad S \underset{CHMe \cdot CO}{\overset{CS\text{------}NPh}{<}}$$

(III.) (IV.)
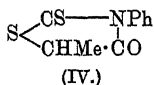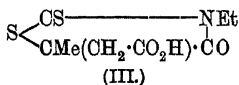
The Quinoline Group.

The well-known reactivity of 2- and 4-substituents in the
pyridine nucleus is further exemplified by the preparation of α-
and γ-quinolinesulphonic acids by boiling the corresponding
chloro-compounds with a solution of sodium hydrogen sulphite.[54]
Similarly, the acids, which may also be prepared from the thio-
quinolines, on treatment with phosphorus pentachloride give, not
the corresponding sulphonyl chlorides, but the chloroquinolines,
and the α-sulphonic acid is converted into carbostyril by simply
boiling it with water. The β-isomeride, which is obtained in an

[52] C. Gränacher, Helv. Chim. Acta, 1920, 3, 152; A., i, 252.
[53] S. Kallenberg, Ber., 1919, 52, [B], 2057; A., i, 90.
[54] E. Besthorn and B. Geisselbrecht, ibid., 1920, 53, [B], 1017; A., i, 563.

indirect manner, is a stable compound, from which a sulphonyl chloride can be prepared in the usual way.

The total synthesis of quinine and its derivatives is nearing completion, since methods are now available for dealing with particular cases of each stage of the problem. As these may well prove adequate for the purpose in view, it seems appropriate to indicate briefly the present position.

(*a*) The syntheses of quinic and cinchonic acids from quinoline and methoxyquinoline, respectively, have been referred to in previous Reports,[55] whilst the communication is promised of results obtained by the use of Knorr's quinoline synthesis.[56]

(*b*) For the preparation of appropriate derivatives of β-4-piperidylpropionic acid, hitherto certain less valuable alkaloids of the cinchonine group have been subjected to degradation. For example, cinchotine (dihydrocinchonine) (I) is converted into cinchoticine (cinchotoxine) (II). The dimethosulphate of *N*-benzoylcinchotoxine (III) is then converted by oxidation to
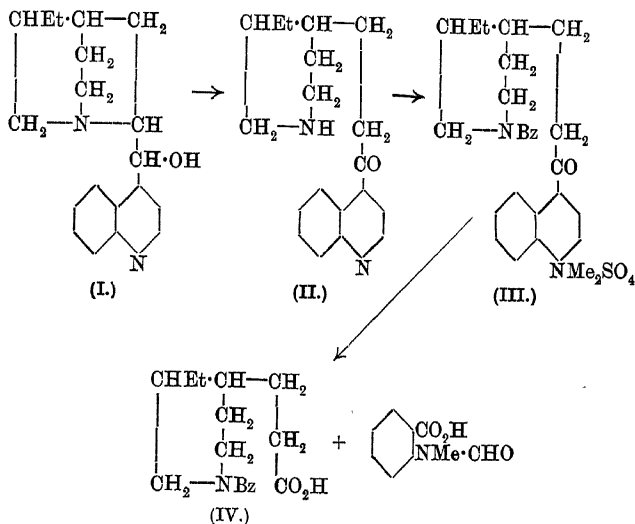
N-benzoylhomocincholoeupone (IV).[57] The synthesis proper of these acids is now foreshadowed by that of the parent β-4-piperidyl-

[55] *Ann. Reports*, 1918, **15**, 113; 1911, **8**, 142.

[56] P. Rabe and K. Kindler, *Ber.*, 1918, **51**, 1360; *A.*, 1919, i, 34.

[57] A. Kaufmann, E. Rothlin, and P. Brunnschweiler, *ibid.*, 1916, **49**, 2299; *A.*, 1917, i, 50; P. Rabe and K. Kindler, *loc. cit.*

propionic acid as the product of reduction of β-4-pyridylacrylic acid, which may be obtained from γ-picoline and chloral:
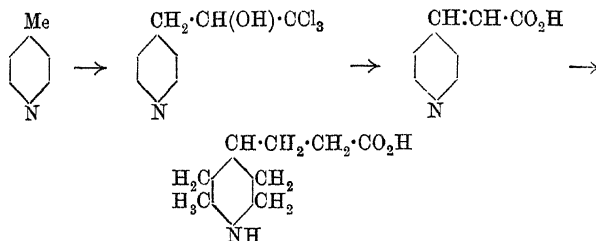
Since it has also been found possible to convert nicotinic acid into β-ethylpyridine,[58] there is a good prospect of preparing homo-cincholeupone from γ-picoline-β-carboxylic acid, which itself is accessible by synthesis. Owing, however, to the presence of two asymmetric carbon atoms in the formula, the synthetic product will consist of four isomerides, of which only one will serve for the synthesis of the natural alkaloids. Further, special precautions will, of course, be required in connexion with the unsaturated group when the attempt is made to synthesise homomeroquinenine, from which cinchonine and quinine themselves are derived.

(c) The condensation of ethyl cinchonate or ethyl quinate with ethyl N-benzoylhomocincholeupone by means of the Claisen reaction, and subsequent elimination of the benzoyl and carbethoxyl groups, has resulted in the respective syntheses of dihydrocinchoticine [59] (I) and dihydroquinicine,[59a] which have been con-

(I.)
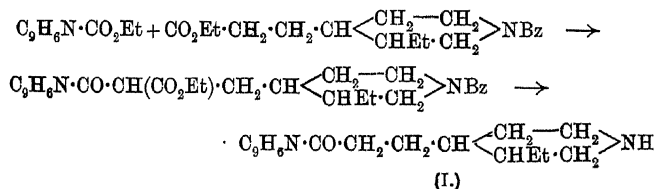
verted by known methods [60] into dihydrocinchoninone and dihydroquininone respectively. From these ketones, dihydrocinchonine and dihydrocinchonidine on the one hand, and dihydroquinine and dihydroquinidine on the other, are produced by reduction in the same manner as quininone yields quinine and quinidine.

[58] P. Rabe and K. Kindler, loc. cit.   [59] Ibid.
[59a] Ibid., Ber., 1919, 52, [B], 1842; A., i, 78.
[60] Ann. Reports, 1918, 15, 113.

The structure of cinchonine being clear, the greater prospect of determining those of its isomerides has led to renewed investigations of their relationships to the alkaloid. Apart from cinchonidine, the stereoisomerism of which with cinchonine is represented by the formulæ (I) and (II),[61] and the ketone

$$CH_2{:}CH{\cdot}CH{-}CH{-}CH_2$$
$$CH_2{:}CH{\cdot}CH{-}CH{-}CH_2$$
$$\quad{-}CH{-}CH{-}CH_2$$
$$| \quad CH_2 \quad | \qquad | \quad CH_2 \quad | \qquad | \quad CH_2 \quad |$$
$$| \quad CH_2 \quad | \qquad | \quad CH_2 \quad | \qquad | \quad CH_2 \quad |$$
$$CH_2{\cdot}N{-}CH \qquad CH_2{\cdot}N{-}CH \qquad CH_2{\cdot}N{-}CH$$
$$HO{\cdot}CH \qquad\qquad H{\cdot}C{\cdot}OH \qquad\quad {-}C_2H_4{-}O{-}CH$$

(I.)   (II.)   (III.)
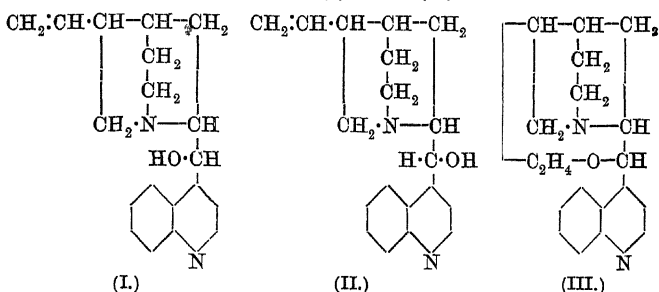
cinchotoxine, there are known α-*iso*cinchonine (cinchoniline), β-*iso*cinchonine (cinchonigine), and *apo-* or *allo*-cinchonine. These are all derived from cinchonine by the action of hydro-haloid or sulphuric acids, or by elimination of the elements of the hydrogen haloids from its hydro-haloid additive products. *apo*Cinchonine, like cinchonine itself, reacts as an unsaturated hydroxylic compound, but the others do not, and have therefore been considered to be internal ethers.[62] This has been confirmed in the case of the α-isomeride, which is stable towards dilute mineral acid, but is converted by dilute acetic or phosphoric acids into a hydroxy-dihydrocinchotoxine (IV), from which a hydroxydihydrocinchoninone (V) can be obtained by the general reaction previously mentioned.[63] The structure of cinchoniline is therefore repre-

$$HO{\cdot}C_2H_4{\cdot}CH{-}CH{-}CH_2 \qquad\qquad HO{\cdot}C_2H_4{\cdot}CH{-}CH{-}CH_2$$
$$| \quad CH_2 \quad | \qquad\qquad\qquad\qquad | \quad CH_2 \quad |$$
$$| \quad CH_2 \quad | \qquad \longrightarrow \qquad | \quad CH_2 \quad |$$
$$CH_2{\cdot}NH \;\; CH_2 \qquad\qquad\qquad CH_2{\cdot}N{-}CH$$
$$\qquad\qquad CO \qquad\qquad\qquad\qquad\qquad\qquad CO$$

(IV.)   (V.)

[61] P. Rabe and others, *Annalen*, 1910, 373, 85; *A.*, 1910, i, 417.
[62] W. Koenigs, *ibid.*, 1906, 347, 185; *A.*, 1906, i, 762.
[63] P. Rabe and B. Böttcher, *Ber.*, 1917, 50, 127; *A.*, 1917, i, 281.

sented by the formula (III), the nature of the group $\cdot C_2H_4\cdot$ being left undetermined. On other grounds, however, this would appear to have the ethylidene structure, since α-hydroxydihydrocinchonine gives the iodoform reaction, and therefore probably contains the grouping $CH_3\cdot CH\cdot OH\cdot$.[64] This compound, which is obtained by the addition of the elements of water to cinchonine, is probably stereoisomeric with the β-compound, produced simultaneously, since both on dehydration give α- and β-*iso*cinchonines and *apo*cinchonine, although in relative proportions, which are not the same in each case.[65] Further, although the three isomerides of cinchonine, on treatment with hydrogen bromide, form the same hydrobromocinchonine, this is accompanied in the cases of β-*iso*cinchonine and *apo*cinchonine by hydrobromo-*apo*cinchonine. Also cinchonine and α-*iso*cinchonine give the same hydroiodocinchonine, but β-*iso*cinchonine and *apo*cinchonine give hydroiodo-*apo*cinchonine. It is therefore concluded that α-*iso*cinchonine is sterically related to cinchonine and β-*iso*cinchonine to *apo*cinchonine, the relationship of the isomerides being expressed by the formulæ: [66]

$$CH_2\mathord{:}CH\cdot C_{16}H_{17}N_2\mathord{:}CH\cdot OH$$

Cinchonine.

$$CH_3\cdot CH\cdot C_{16}H_{17}N_2\mathord{:}CH$$
$$\underline{\qquad O\qquad}$$

Cinchonigine and cinchoniline.

$$CH_3\cdot CH\mathord{:}C_{16}H_{16}N_2\mathord{:}CH\cdot OH$$

*apo*Cinchonine.

By treatment of cinchonidine with sulphuric acid, there results, besides β- and *apo*cinchonidines, a hydroxydihydrocinchonidine, which gives the iodoform reaction, and on dehydration furnishes β- and *apo*cinchonidines but no internal ether. This deviation from the behaviour of the hydroxydihydrocinchonines leads to the suggestion of structurally distinct formulæ for the hydroxy-dihydro-derivatives of cinchonidine and cinchonine.[67] These, however, need not be reproduced here, since the reader will probably find it difficult to reconcile this view with the stereoisomeric relationship of cinchonine to cinchonidine. The writer prefers to consider the difference in question as explicable by assigning the formula (I) to cinchonine, leaving the formula (II) for cinchonidine.

[64] E. Léger, *Compt. rend.*, 1918, **166**, 903; *A.*, 1918, i, 304.

[65] *Idem, ibid.*, 1919, **168**, 404; *A.*, 1919, i, 170.

[66] *Idem, ibid.*, 1918, **166**, 255, 469; *A.*, 1918, i, 182, 232.

[67] *Idem, ibid.*, 1919, **169**, 67; *A.*, 1919, i, 451.

Quinoline Dyes.

The constitution of the *iso*cyanines has been variously represented by the formulæ (I), (II), and (III):

(I.)   (II.)

(III.)   (IV.)

of which (II) alone explains the formation of identical products from unsubstituted quinolines and from their 4-chloro-derivatives.[68] Against (III), it has been shown[69] that the methiodide of the synthetic product (IV) resulting from the reduction of the condensation product of *o*-nitrocinnamaldehyde and quinaldine differs entirely in its properties from the *iso*cyanines. Furthermore, dimethyl*iso*cyanine acetate, on oxidation, yields 1-methyl-2-quinolone and cinchonic acid methochloride (hydrochloric acid being used in separating the two).[70] It will be seen that this result favours a formula of the type (V) rather than (II) for the
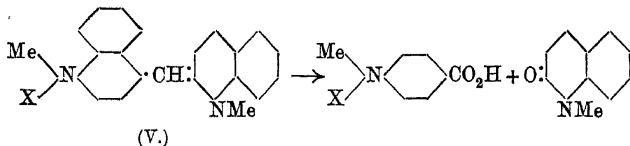
(V.)
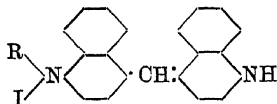
(VI.)

[68] A. Kaufmann and E. Vonderwahl, *Ber.*, 1912, **45**, 1404; *A.*, 1912, i, 502.
[69] W. H. Mills and P. E. Evans, *T.*, 1920, **117**, 1035.
[70] W. H. Mills and R. S. Wishart, *ibid.*, 579.

*iso*cyanines, but it is probable that the two represent virtually tautomeric compounds. It is therefore not surprising that dyes of the *iso*cyanine type are also obtainable[71] from the alkyl haloid additive products of sufficiently pure lepidine[72] and its homologues. From analogy, the cyanines almost certainly correspond with the formula (VI).

The constitution of pinacyanol has also been elucidated.[72a] This diethylcarbocyanine is better prepared by the action of potassium hydroxide and formaldehyde on a mixture of the ethiodides of quinoline and quinaldine than on quinaldine ethiodide alone; yet the latter is alone concerned in the reaction. By oxidation of diethylcarbocyanine bromide with dilute nitric acid, quinaldinic acid ethyl nitrate (VII) is produced, whilst by the action of potassium permanganate on the acetate, 1-ethyl-2-quinolone (VIII) is obtained. The formula (IX) is therefore adopted for pinacyanol.
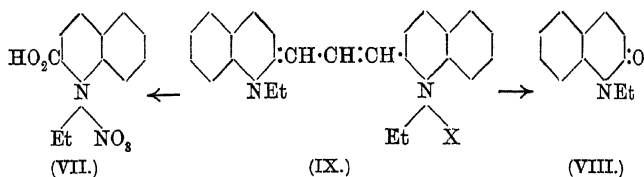
In view of the importance of these compounds in colour photography, and the fact that hitherto their manufacture had been a German monopoly, activity is being displayed in various directions in working out the details of their preparation.[73]

The Chelidonium Alkaloids.

β-Homochelidonine, an isomeride of cryptopine, resembles it in its physiological action, and in that its oxidation by mercuric acetate results in the displacement of two hydrogen atoms by an

[71] E. Q. Adams and H. L. Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2389; *A.*, 1921, i, 53.

[72] L. A. Mikeska, *ibid.*, 2396; *A.*, 1921, i, 54.

[72a] W. H. Mills and (Miss) F. M. Hamer, *T.*, 1920, **117**, 1550; compare O. Fischer, *J. pr. Chem.*, 1918, [ii], **98**, 204; *A.*, 1919, i, 172; L. E. Wise, E. Q. Adams, J. K. Stewart, and C. H. Lund, *J. Ind. Eng. Chem.*, 1919, **11**, 460; *A.*, 1919, i, 416.

[73] H. Barbier, *Bull. Soc. chim.*, 1920, [iv], **27**, 427; *A.*, i, 568; L. E. Wise, E. Q. Adams, J. K. Stewart, and C. H. Lund, *J. Ind. Eng. Chem.*, 1919, **11**, 460; *A.*, 1919, i, 416; L. A. Mikeska, H. L. Haller, and E. Q. Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 2392; *A.*, 1921, i, 54; (Sir) W. J. Pope, *J. Soc. Chem. Ind.*, 1920, **39**, 370R.

oxygen atom. It is therefore called *allo*cryptopine, and represented by the formula (II),[74] that for cryptopine being (I):

(I.)

(II.)

(III.)
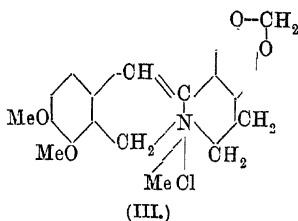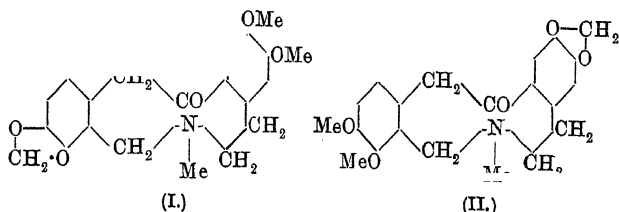
In conformity with this, *allo*cryptopine is converted by treatment with phosphoryl chloride into dihydroberberine methochloride (III), just as *iso*cryptopine chloride is obtained from cryptopine. Similarly, dihydro*allo*cryptopine (IV) gives tetrahydroberberine methochloride (V):

(IV.)

(V.)
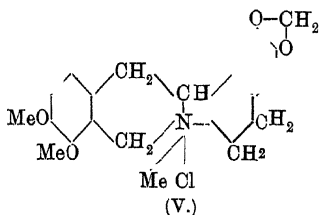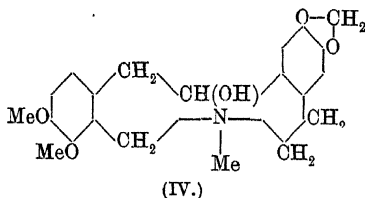
The authors of the formulæ (I and II) have each expressed some misgivings in attributing a ten-membered·ring structure to natural

products. It is, however, now suggested that the salts of these alkaloids, which is the form in which they occur naturally, contain two six-membered rings, and that the ten-membered ring is only produced when the bases are isolated. The changes involved are formulated as follows:
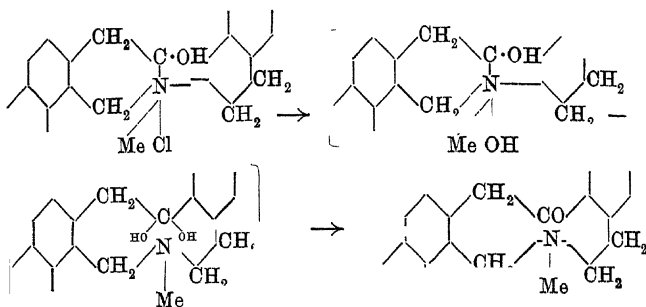
This view readily explains the fact that the bases are only gradually precipitated from solutions of their salts by alkali.

Sufficient progress has been made towards the determination of the constitution of chelidonine and α-homochelidonine to permit the deduction of provisional formulæ for these alkaloids as a working basis. They differ from allocryptopine in that on oxidation with mercuric acetate, they merely lose two atoms of hydrogen. The reaction serves, however, to connect these compounds with chelerythrine, since the product from α-homochelidonine has been identified as dihydrochelerythrine.

Codeine.

A considerable advance towards the determination of the constitution of codeine and its congeners has been made by the preparation of two structurally distinct forms of tetrahydrodeoxycodeine.[75] Of these, the α-form, which had been previously obtained from deoxycodeine by means of sodium and alcohol, was considered to be a dihydro-derivative, but its formation from codeine by the following series of reactions:

$$C_{18}H_{21}O_3N \xrightarrow[\text{(Pd.)}]{H_2} C_{18}H_{23}O_3N \xrightarrow{PCl_5} C_{18}H_{22}O_2NCl \xrightarrow[\text{(electrolytic)}]{H_2}$$

Codeine. Dihydrocodeine. Chlorodihydrocodide.

$$C_{18}H_{23}O_2N \xrightarrow[\text{(Pd.)}]{H_2} C_{18}H_{25}O_2N,$$

Dihydrodeoxy-   α-Tetrahydro-
codeine.   deoxycodeine.
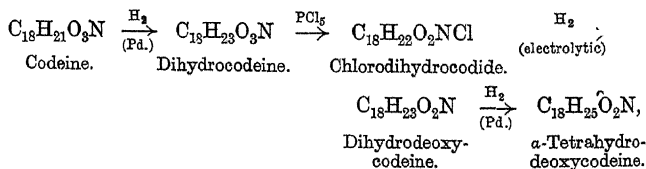
[75] M. Freund, W. W. Melber, and E. Schlesinger, *J. pr. Chem.*, 1920, [ii], **101,** 1; *A.*, i, 757.

leaves no doubt as to its composition. The absorption by deoxy-codeïne of two molecular proportions of hydrogen in the presence of palladium is equally conclusive in respect of the β-compound. Of the two formulæ current for codeine, the first (I) [76] affords no

(I.)   (II.)
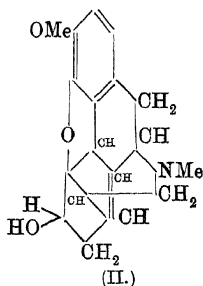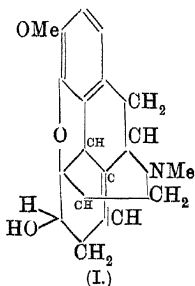
explanation of the isomerism, but according to the second (II) [77] the changes may be represented in the following way:

Deoxycodeine.
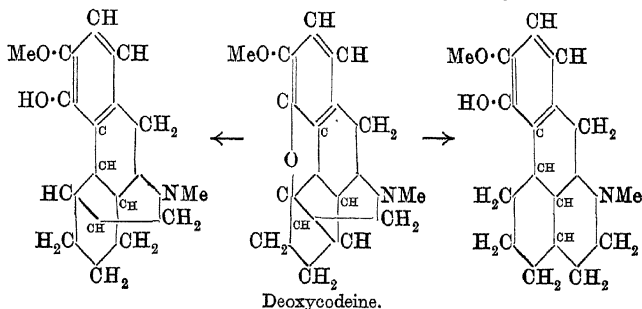
Both the tetrahydro-derivatives contain phenolic hydroxyl groups, but it is to be noted that there is at present no evidence which permits a decision as to which of the two formulæ is to be attributed to either compound.

Pyrrolidine Alkaloids.

Cuskhygrine, to which the formula (I) was assigned [78] on the grounds of its empirical composition and its oxidation to hygric acid (A), is in reality $a\gamma$-di-N-methyl-2-pyrrolidylpropan-β-one (II).[79] Its asymmetry follows from the formation of two distinct

[76] L. Knorr and H. Hörlein, *Ber.*, 1907, **40**, 3341; *A.*, 1907, i, 789; compare J. von Braun, *Ber.*, 1914, **47**, 2312; *A.*, 1914, i, 1138.

[77] M. Freund and E. Speyer, *ibid.*, 1916, **49**, 1287; *A.*, 1916, i, 738.

[78] C. Liebermann and G. Cybulski, *ibid.*, 1895, **28**, 585; *A.*, 1895, i, 310.

[79] K. Hess and H. Fink, *ibid.*, 1920, **53**, [B], 781; *A.*, i, 497.

hydrazones, which are notable as the first examples of their kind, and are reduced by sodium ethoxide respectively to di-N-methyl-2-

$$
\begin{array}{cc}
\underset{\underset{\diagdown\diagup}{\underset{NMe}{\overset{\overset{CH_2-CH_2}{|}}{CH_2}}}{CH_2} \underset{\diagdown\diagup}{\overset{CH\cdot CH_2\cdot CO\cdot CH_2\cdot CH}{\underset{NMe}{}}} \overset{CH_2-CH_2}{\underset{\underset{NMe}{CH_2}}{}}
\end{array}
$$
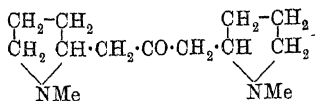
(I.)
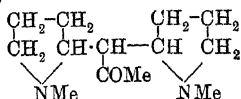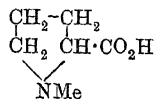
$$
\text{(II.)} \qquad \text{(A.)}
$$

pyrrolidylmethane (IV) and $\alpha\alpha$-di-N-methyl-2-pyrrolidylpropane (V). The alkaloid does not respond to the usual tests for the

(V.) $\qquad \xleftarrow{\alpha\text{-form}} \qquad \qquad \qquad$

$\xrightarrow{\beta\text{-form}}$
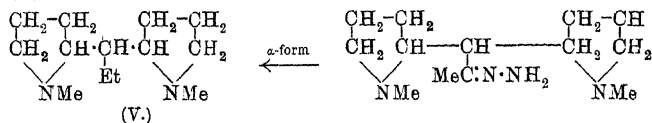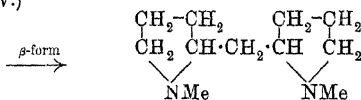
(IV.)

$\cdot CH_2\cdot CO\cdot$ grouping, but absorbs six molecular proportions of nitric oxide in the presence of sodium ethoxide. This reaction has not been utilised since its discovery,[80] but promises to be specially valuable in such cases in that it permits the rupture of the molecule by a smooth alkaline hydrolysis into simpler recognisable fragments. In the present instance there are thus obtained methylenedi*iso*nitroamine, N-methyl-2-pyrrolidylacetic acid, and a mixture of unsaturated, more or less completely demethylated, bases of the type (VI), which by reduction and re-methylation give the above di-N-methyl-2-pyrrolidylmethane as sole product:

$\longrightarrow$

$CH_2(N_2O_2H)_2 \; + \;$ 　　　　　$+$
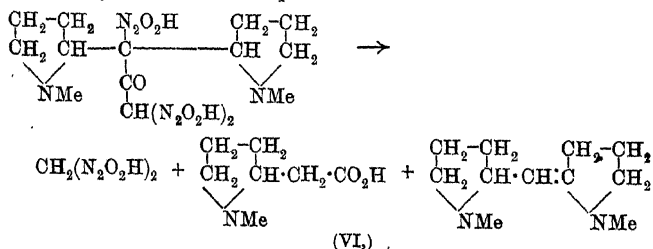
(VI.)

[80] W. Traube, *Annalen*, 1898, **300**, 81 ; *A.*, 1898, i, 349.

By the action of potassium hydroxide, cuskhygrine is converted into hygrine. It is suggested that a similar reaction may occur in nature, and further that the carboxyl group of ecgonine may represent an oxidised pyrrolidine nucleus of cuskhygrine.

A reaction [81] which may well render the synthesis of cocaine and related compounds a commercial possibility consists in the application of the Dieckmann reaction to diethyl N-methyl-2 : 5-pyrrolidyldiacetate, which is obtained by the action of methylamine on diethyl succinyldiacetate. The condensation product thus obtained is then reduced in glacial acetic acid solution by hydrogen in the presence of platinum:

$$
\begin{array}{cc}
\begin{array}{l}
CH_2 \cdot CO \cdot CH_2 \cdot CO_2Et \\
CH_2 \cdot CO \cdot CH_2 \cdot CO_2Et
\end{array} + CH_3 \cdot NH_2 \longrightarrow &
\begin{array}{l}
CH\text{:}C \cdot CH_2 \cdot CO_2Et \\
NMe \\
CH\text{:}C \cdot CH_2 \cdot CO_2Et
\end{array} \longrightarrow
\end{array}
$$

$$
\begin{array}{cc}
\begin{array}{l}
CH_2 \cdot CH \cdot CH_2 \cdot CO_2Et \\
\quad NMe \\
CH_2 \cdot CH \cdot CH_2 \cdot CO_2Et
\end{array} &
\begin{array}{l}
CH_2 \cdot CH\!-\!CH \cdot CO_2Et \\
\quad NMe \;\; CO \\
CH_2 \cdot CH\!-\!CH_2
\end{array}
\end{array}
$$
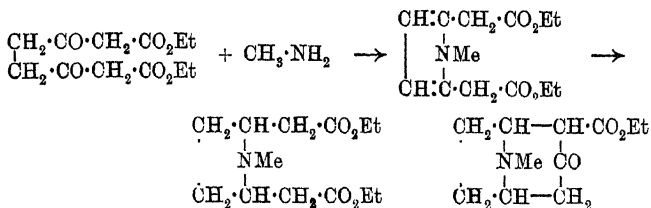
The ethyl tropinonecarboxylate produced may be reduced electrolytically or by sodium amalgam to the ethyl ester of r-ecgonine.

The constitution of scopolamine and scopoline has now been determined. As scopoline was known to be an internal ether, from which hydroscopoline (1 : 2-dihydroxytropan),[82] A, was

$$
\begin{array}{c}
\overset{4}{C}H_2\text{-}\overset{5}{C}H_2\text{-}\overset{6}{C}H_2 \\
\overset{3}{C}H \cdot NMe \cdot \overset{7}{C}H \\
\underset{2}{C}H(OH)\!-\!\underset{1}{C}H \cdot OH \\
A.
\end{array}
$$
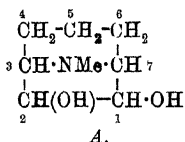
derived by rupture of the etheric linkage [83] through the addition of two hydrogen atoms, it only remained to determine which of the other atoms of the molecule is involved in the oxide ring. The remarkable results of the degradation of scopoline by exhaustive methylation permit a decision on this point.[84] Although the distillation of scopoline methohydroxide under ordinary pressure results in profound decomposition,[85] under diminished pressure satisfactory

[81] R. Willstätter, *D.R.-P.* 302401; *A.*, i, 680.

[82] *Ann. Reports*, 1918, **15**, 112.

[83] E. Schmidt, *Apoth. Zeit.*, 1902, **17**, 592; *A.*, 1903, i, 51.

[84] K. Hess, *Ber.*, 1919, **52**, [B], 1947; *A.*, i, 81.

[85] W. Luboldt, *Arch. Pharm.*, 1898, **236**, 26; *A.*, 1898, i, 499; E. Schmidt, *Arch. Pharm.*, 1905, **243**, 566; *A.*, 1906, i, 103.

results are obtained. In place of the expected product, however, an isomeric, doubly unsaturated tertiary base, ψ-demethylscopoline (II), is obtained. The crucial result follows from the attempt to degrade this compound by exhaustive methylation, and may be considered in the following manner, which differs somewhat from that in the original paper. The product has a molecular formula greater by one methylene group than that of ψ-demethylscopoline, due to the presence of a methoxy-group. The double bonds present have no influence on the result, because the product gives a tetra-hydro-derivative (IV), which is identical with that similarly obtained from tetrahydro-ψ-demethylscopoline (V). Although a free hydroxyl group is no longer present, it cannot be assumed that direct methylation of the hydroxyl group in ψ-demethylscopoline has occurred under such conditions. Hence the oxygen atom of the etheric linkage must have been methylated as the result of a profound molecular rearrangement, the product therefore being called O-methyl*iso*-ψ-demethylscopoline (III). Such a change, how-ever, can only be adequately explained by assuming that the dimethylamino-group of ψ-demethylscopoline is attached to one of the carbon atoms carrying the etheric linkage, which is destroyed so easily. This atom must therefore be 3- or 7- of the tropine ring. Assuming that the other carbon atom involved in the ether struc-ture is that in position 2, the former is excluded because it would involve the initial formation of a double bond in the original degradation of N-methylscopoline either in the 1 : 7- or the 6 : 7-posi-tions. Of these, the first would represent the formation of the enolic form of a ketone, which is not observed, and the second supplies no explanation of the instability of the initial product and its rearrangement to a doubly unsaturated compound. This, how-ever, is at once forthcoming on the assumption that the dimethyl-amino-group of ψ-demethylscopoline is attached to the 7-carbon atom, as will be seen from the scheme on p. 129. The formula for scopoline is therefore represented by (I), whilst that for scopolamine is (VI).

One of the two quaternary carbon atoms is seen to be responsible for each of the rearrangements. It is noteworthy that both O-methyl*iso*-ψ-demethylscopoline and its tetrahydro-derivative are recovered unchanged when the attempt is made to degrade them further by exhaustive methylation.

The results of this investigation are an excellent illustration of the valuable information as to the factors which modify the stability of cyclic compounds to be derived from a study of natural

CH₂·CH₂·CH₂
| |
CH·NMe·C   →
|_/⎺O⎺_|
OH⎯⎯⎯CH·OH
(I.)

[CH₂·CH₂·CH₂]
| |
CH   C·NMe₂   →
‖_/⎺O⎺\
C⎯⎯⎯CH·OH

CH₂:CH·CH₂
| |
CH₂   C·NMe₂⎯
‖_/⎺O⎺_|
C⎯⎯⎯CH·OH
(II.)

→
[CH₂·CH·CH₂]
| |
CH₂   C(OH)·NMe₂
| |
C(OMe)⎯CH·OH

CH₂:CH·CH₂
| |
CH₂   C·NMe₂
‖ |>O
C(OMe)⎯⎯CH
(III.)

CH₃·CH₂·CH₂
| |
CH₃   C·NMe₂
| |>O
CH(OMe)·CH
(IV.)

CH₂·CH₂·CH₂
| |
CH·NMe·C
|_/⎺O⎺_|
CH⎯⎯⎯CH·O·CO·CHPh·CH₂·OH
(VI.)

CH₃·CH₂·CH₂
| |
CH₃   C·NMe₂⎯
|_/⎺O⎺_|
CH⎯⎯⎯CH·OH
(V.)
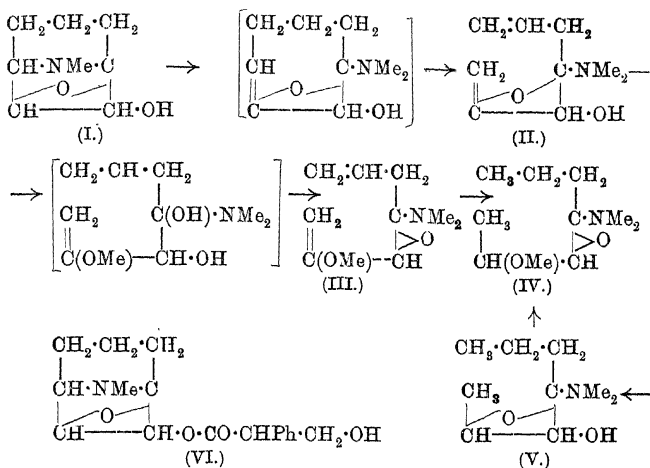
products—made up as they often are of structures not obtainable in the laboratory.

J. KENNER.

ANALYTICAL CHEMISTRY.

THE contributions to this branch of chemistry have been of a much more varied character during the past year than has been the case during the preceding five years. America has continued to show the greatest activity in this respect, whilst the conditions in this and other countries more seriously affected by the war have not yet become normal.

The main material difficulties in the way of analytical work have been the lack of an adequate supply of suitable glass apparatus and the continued shortage of platinum. Further devices have, therefore, been proposed to obviate the use of that metal.[1] For example, it has been shown that for certain quantitative estimations, such as the analysis of chrome iron ore, platinum basins may be replaced by lead basins;[2] whilst iron basins are suitable for sulphide fusions.[3] An efficient substitute for platinum wire for flame tests may be prepared from a strip of rolled filter paper,[4] or from the " lead " of a black-lead pencil.[5]

Physical Methods.

A new form of viscosimeter of the capillary type has been devised. The oil or other liquid is forced up into the tube by the compression of a bulb, the temperature brought to a definite point by means of a thermostatic jacket, and the time required for the liquid to fall between given points is noted. The absolute vicosity is then calculated by means of the formula: $\eta = Kdt$, where K represents a constant of the apparatus, d the specific gravity of the liquid, and t the time in seconds.[6]

The errors associated with the falling sphere type of viscosimeter have been taken into consideration in a new instrument,

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[1] Compare *Ann. Reports*, 1918, **15**, 118 ; 1919, **16**, 127.
[2] C. Hütter, *Zeitsch. angew. Chem.*, 1919, **32**, 380 ; *A.*, ii, 189.
[3] H. Sertz, *ibid.*, 1920, **33**, i, 156.
[4] A. Ehringhaus, *Centr. Min.*, 1919, 192 ; *A.*, ii, 263.
[5] C. C. Kiplinger, *J. Ind. Eng. Chem.*, 1920, **12**, 500 ; *A.*, ii, 381.
[6] G. Baume and H. Vigneron, *Ann. Chim. anal.*, 1919, [ii], **1**, 379 ; *A.*, ii, 92.

in which the steel ball is delivered into the centre of the tube, and corrections for the wall and end effects are applied, the result being calculated into absolute viscosity by means of a modification of Stokes' equation.[7]

Fischer's viscosimeter, which is particularly suitable for very viscid liquids, consists essentially of an inner tube surrounded by a water jacket, resembling a vertical Liebig's condenser, through which water at a definite temperature is run. The viscosity is measured by the time required by a metal ball to fall between two points on the inner tube.[8]

A viscosimeter may be used for determining the density of a liquid of which only a few c.c. are available,[9] the calculation being made by a combination of the formulæ of Ostwald-Poiseuille and of Scarpa.[10]

The determination of the surface tension affords a means of identifying minute quantities of organic liquids. A capillary tube containing a short column of the liquid is turned until the lower meniscus of the latter changes to a plane surface, and the angular deviation of the tube from the vertical position is then read on a quadrant scale. The surface tension, T, is calculated by means of the usual formula: $T = d \times h \times r \times 980/2$ dynes per sq. cm.[11]

For estimating the acidity of liquids, the use of surface-active indicators, as originally suggested by Traube and Somogyi,[12] is often more convenient than the use of colour indicators.[13] By using salts of alkaline nature, such as eucupine dihydrochloride, it is possible to titrate highly dissociated acids in the presence of a primary phosphate,[14] whilst the relative alkalinity of the carbonates and hydrogen carbonates of potassium, sodium, calcium, and magnesium may be determined in an analogous manner.[15]

A study of the soap-bubble method of determining the ignition temperature of gaseous mixtures[16] has shown that, even after careful standardisation of the coils, size of bubble, and other details, the results cannot be depended on, even for comparative purposes.[17]

[7] W. H. Gibson and (Miss) L. M. Jacobs, *T.*, 1920, **117**, 473.

[8] *Chem. Zeit.*, 1920, **44**, 622.

[9] W. Block, *Zeitsch. angew. Chem.*, 1920, **33**, 198; *A.*, ii, 590.

[10] *Gazzetta*, 1910, **40**, ii, 261; *A.*, 1911, ii, 17.

[11] C. C. Kiplinger, *J. Amer. Chem. Soc.*, 1920, **42**, 472; *A.*, ii, 291.

[12] *Int. Zeitsch. phys.-chem. Biol.*, 1914, **1**, 479; *A.*, 1915, ii, 101.

[13] W. Windisch and W. Dietrich, *Biochem. Zeitsch.*, 1919, **100**, 130; *A.*, ii, 48.

[14] *Ibid.*, 135; *A.*, ii, 706.   [15] *Ibid.*, **101**, 82; *A.*, ii, 707.

[16] J. W. McDavid, *T.*, 1917, **111**, 1003.

[17] A. G. White and T. W. Price, *ibid.*, 1919, **115**, 1248.

The melting-point curves obtained with binary and ternary mixtures of nitronaphthalenes may be used in the analysis of the industrial products of nitration. The simultaneous presence of mono- and tri-nitronaphthalene is indicated by points of arrest in the cooling curves.[18] Even when the melting point of the pure substance is not known, the freezing-point curve affords an indication of the amount of impurity present.[19]

A new physico-chemical method of examining double salts has been based on the measurement of the temperature produced on mixing the solutions with a constant liquid, such as phenol. When a double salt is in solution, there is a variable difference between the observed and calculated results.[20]

Turning to optical methods, it has been shown that the ion content of an aqueous solution of salts may be calculated from the refractive indices of the liquid before and after precipitation of one of the component salts.[21]

Small amounts of lead in copper may be estimated spectroscopically,[22] the time required for the bright lead line ($405 \cdot 8 \ \mu\mu$) under constant conditions being noted. Another application of spectrophotometry is in the analysis of colourless organic compounds, which for this purpose are converted into coloured compounds.[23]

Reference may also be made to a new form of nephelometer[24] and to a photographic turbidimeter, in which one beam of light is passed through the column of suspended substance and a second beam of equal intensity through standardised glass disks.[25] In the nephelometric estimation of chlorides, the intensity of the opalescence of the silver chloride suspension is increased and rendered more constant by heating the liquid to 40° after the precipitation.[26] The nephelometric values of cholesterol and the higher fatty acids have been shown to be affected by hydrolysis and by the presence of other substances, which, by themselves, do not produce turbidity.[27]

The comparison of the fluorescence produced by ultra-violet rays

[18] P. Pascal, *Bull. Soc. chim.*, 1920, [iv], **27**, 388 ; *A.*, ii, 514.

[19] W. P. White, *J. Physical Chem.*, 1920, **24**, 393 ; *A.*, ii, 529.

[20] R. Dubrisay, *Compt. rend.*, 1920, **170**, 1582 ; *A.*, ii, 508.

[21] M. de Crinis, *Zeitsch. physiol. Chem.*, 1920, **110**, 254 ; *A.*, ii, 700.

[22] C. W. Hill and G. P. Luckey, *Trans. Amer. Electrochem. Soc.*, 1917, **32**, 335 ; *A.*, ii, 193.

[23] W. E. Mathewson, *J. Amer. Chem. Soc.*, 1920, **42**, 1277 ; *A.*, ii, 566.

[24] C. Chéneveau and R. Audubert, *Compt. rend.*, 1920, **170**, 726 ; *A.*, ii, 327.

[25] W. G. Bowers and J. Moyer, *J. Biol. Chem.*, 1920, **42**, 191 ; *A.*, ii, 444.

[26] A. B. Lamb, P. W. Carleton, and W. B. Meldrum, *J. Amer. Chem. Soc.*, 1920, **42**, 251 ; *A.*, ii, 383.

[27] F. A. Csonka, *J. Biol. Chem.*, 1920, **41**, 243 ; *A.*, ii, 272.

on substances in the cylinders of a nephelometer affords a new means of quantitative analysis.[28]

A physical method of identifying and determining the purity of acids has been based on the observation of their dissociation constant, which may be determined, for example, by comparing the change of colour of the same indicator in the solution and in a standard solution of known hydrogen-ion concentration.[29] A simple method of determining the ion concentration of ultra-filtrates and other solutions free from proteins is to add an ion forming a sparingly soluble salt with the ion in question, and to note the limit of solubility, as indicated by the formation of a milky turbidity. In the case of calcium, the method gives results accurate within 2 to 3 milligrams per litre.[30]

A method of analysis by fractional distillation under a constant reduced pressure is useful for the separation of substances having boiling points which are close together. The fractionation is continued until the final fractions show, not only identical boiling points, but also agree in their other physical properties, such as density, refractive index, and viscosity.[31]

Gas Analysis.

Various instruments for the automatic analysis of gases or for the detection of an individual constituent have been described. The katharometer, which is intended for the estimation of small quantities of hydrogen in air, is based on the change in the electrical resistance of a platinum helix through the increase in temperature caused by surface combustion of the hydrogen.[32] An analogous principle has been utilised in the estimation of carbon monoxide in air.[33]

The thermal conductivity method can only be applied quantitatively when the probable identity and amounts of constituents likely to be present in a gaseous mixture are known, but under such conditions it gives good results in many cases.[34]

[28] L. J. Desha, *J. Amer. Chem. Soc.*, 1920, 42, 1350 ; *A.*, ii, 552.

[29] I. M. Kolthoff, *Pharm. Weekblad*, 1920, 57, 514 ; *A.*, ii, 628.

[30] R. Brinkman and (Miss) E. van Dam, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 762 ; *A.*, ii, 510.

[31] C. Moureu, C. Dufraisse, and P. Robin, *Bull. Soc. chim.*, 1920, [iv], 27, 523 ; *A.*, ii, 562.

[32] H. A. Daynes and G. A. Shakespear, *Proc. Roy. Soc.*, 1920, 97, [A], 273 ; *A.*, ii, 503.

[33] A. B. Lamb and A. T. Larson, *J. Amer. Chem. Soc.*, 1919, 41, 1908 ; *A.*, ii, 126.

[34] E. R. Weaver and P. E. Palmer, *J. Ind. Eng. Chem.*, 1920, 12, 894 ; *A.*, ii, 701.

Another instrument which may be used for the estimation of small amounts of hydrogen or helium in air is the interferometer, which measures the difference in the refractivity of two gases.[35]

A weighing burette for use in gas analysis has been devised, the weight of the gas and alterations in volume caused by the absorption of the constituents being determined by weighing the quantity of mercury which is removed from, or introduced into, the burette.[36] Improved modifications of Orsat's apparatus have also been described.[37, 38]

A source of error in the analysis of gases by fractional combustion with copper oxide is the dissociation of the latter, with the liberation of oxygen. This may be obviated by subsequently passing the nitrogen repeatedly over the oxide at a moderate red heat.[39]

The use of an ammoniacal copper solution has several advantages over alkaline pyrogallol as an absorbent for the estimation of oxygen. If the usual ammonium carbonate solution be replaced by saturated ammonium chloride solution, the gas will be free from carbon dioxide derived from the reagent.[40] On the other hand, when freshly prepared, it may impart traces of ammonia to the gas, and cannot be used in the case of gases containing carbon monoxide or acetylene.[41]

For the estimation of the latter, good results may be obtained, under certain conditions, by the use of ammoniacal cuprous chloride solution as absorption reagent, the solution being then acidified with acetic acid, and the cuprous acetylide separated and estimated.[42] Another suitable reagent for the absorption of acetylene is a solution of mercuric cyanide in sodium hydroxide solution. This effects its separation from ethylene and benzene vapour. For the absorption of ethylene in the presence of benzene, a solution of mercuric nitrate in dilute nitric acid saturated with sodium nitrate may be used.[43] Ilosvay's reagent[44]

[35] J. C. McLennan and R. T. Elworthy, *Trans. Roy. Soc. Canada*, 1919, **13**, [iii], 19 ; *A.*, ii, 508.

[36] E. R. Weaver and P. G. Ledig, *J. Amer. Chem. Soc.*, 1920, **42**, 1177 ; *A.*, ii, 502.

[37] T. B. Smith, *Gas World*, 1919, **71**, 379 ; *A.*, ii, 263.

[38] G. W. Jones and F. R. Neumeister, *Chem. and Met. Eng.*, 1919, **21**, 734 ; *A.*, ii, 119.

[39] E. Ott, *J. Gasbeleucht.*, 1919, **62**, 89 ; *A.*, ii, 52.

[40] W. Haehnel and M. Mugdan, *Zeitsch. angew. Chem.*, 1920, **33**, 35 ; *A.*, ii, 191.

[41] W. L. Badger, *J. Ind. Eng. Chem.*, 1920, **12**, 161 ; *A.*, ii, 264.

[42] J. A. Muller, *Bull. Soc. chim.*, 1920, [iv], **27**, 69 ; *A.*, ii, 198.

[43] W. D. Treadwell and F. A. Tauber, *Helv. Chim. Acta*, 1919, **2**, 601 ; *A.*, ii, 61.   [44] *Ber.*, 1899, **32**, 2697; *A.*, 1900, ii, 52.

removes acetylene quantitatively from coal gas or air, and good results may be obtained by igniting the precipitate with nitric acid and weighing the copper oxide. Hydrogen sulphide must not be present, and in the case of air containing not more than 0·04 per cent. of acetylene, about 5 per cent. of carbon dioxide must be added to prevent oxidation.[45] Methods depending on the reaction of acetylene with silver nitrate, and titration of the liberated nitric acid, are inaccurate, owing to the impossibility of controlling the conditions of the reaction. Good results may be obtained, however, by causing the copper acetylide, separated with Ilosvay's reagent, to react with a sulphuric acid solution of ferric sulphate, and titrating the resulting ferrous sulphate.[46]

A satisfactory reagent for the absorption of carbon monoxide may be prepared by reducing cupric chloride in acid solution by means of stannous chloride. The presence of a slight excess of the latter prevents oxidation by the air, and the reagent may be renewed by expelling the absorbed gas at 60—70°.[47]

A method of detecting and estimating traces of $\beta\beta'$-dichlorodiethyl sulphide (mustard gas) in air has been based on its reducing action on a solution of selenious acid in sulphuric acid, the amount of the orange-red suspension of selenium being estimated by nephelometric comparison with standard suspensions. The selenious reagent also reacts in the same way with arsines and other toxic gases.[48]

Agricultural Analysis.

There has been a considerable amount of investigation as to the most suitable methods of estimating the acidity and the lime requirement of soils. Extraction of an acid soil with potassium nitrate solution, as in the method of Hopkins and Pettit, has been shown to give the same results as extraction with equivalent solutions of potassium chloride, sodium nitrate, sodium chloride, or calcium chloride, whilst variations in the temperature between 25° and 90° do not affect the acidity of the extract. There is little, if any, exchange of acid radicles during the extraction.[49]

[45] H. Arnold, E. Möllney, and F. Zimmermann, *Ber.*, 1920, **53**, [B], 1034 ; *A.*, ii, 513.

[46] R. Willstätter and E. Maschmann, *ibid.*, 939 ; *A.*, ii, 514.

[47] F. C. Krauskopf and L. H. Purdy, *J. Ind. Eng. Chem.*, 1920, **12**, 158 ; *A.*, ii, 267.

[48] M. Yablik, G. St. J. Perrott, and N. H. Furman, *J. Amer. Chem. Soc.*, 1920, **42**, 266 ; *A.*, ii, 272.

[49] H. G. Knight, *J. Ind. Eng. Chem.*, 1920, **12**, 340 ; *A.*, i, 468.

For estimating the lime requirement, the vacuum method [50] gives trustworthy results agreeing with those obtained by the use of a hydrogen electrode after a specified period of shaking, whilst in the case of limed soils the reduction in the acidity is best ascertained by the hydrogen electrode method or the Hopkins method.[51] The method of estimating the acidity or alkalinity of a soil in terms of P_H [52] has been adapted for use in field tests, and a table has been constructed showing the reactions of the soil corresponding with the colour changes of a series of indicators, each of which overlaps the next in the scale.[53]

For the estimation of the total calcium in soils, a method has been devised in which the precipitation with ammonia, and consequent occlusion of calcium in the precipitate, are eliminated. The precipitation is effected by adding solid ammonium oxalate to the boiling solution, which has been rendered first just alkaline with ammonia, and then just acid with hydrochloric acid, and manganese is subsequently separated from the precipitated oxalate.[54] In an investigation of ten different methods of estimating calcium in calcite, the most accurate results were obtained by precipitation as calcium oxalate and weighing as calcium oxide, by precipitation as oxalate from a slightly acid solution, and by the residual titration method.[55]

The small amounts of manganese in plant ashes and similar products can only be estimated colorimetrically. Of the different methods suggested, only that of Marshall [56] has been found to give trustworthy results.[57] In that method, the manganese is oxidised to permanganate by means of potassium persulphate. The influence of various factors on the estimation of chlorides in soil has been studied, and it has been shown that Volhard's method gives more accurate and concordant results than Mohr's method.[58]

For estimating carbonates in limestones, marl, and soil, the method of Van Slyke [59] is the most suitable for substances poor in

[50] J. W. Ames and C. J. Schollenberger, *J. Ind. Eng. Chem.*, 1916, **8**, 243; *A.*, 1916, i, 459.

[51] H. G. Knight, *ibid.*, 1920, **12**, 457, 559; *A.*, i, 587; ii, 557.

[52] E. T. Wherry, *J. Washington Acad. Sci.*, 1919, **9**, 305; *A.*, 1919, i, 428.

[53] *Ibid.*, 1920, **10**, 217; *A.*, ii, 400.

[54] O. M. Shedd, *Soil Sci.*, 1920, **10**, 1; *A.*, ii, 636.

[55] G. E. Éwe, *Chem. News*, 1920, **121**, 53; *A.*, ii, 557.

[56] *Ibid.*, 1901, **83**, 76; *A.*, 1901, ii, 350.

[57] D. H. Wester, *Rec. trav. chim.*, 1920, **39**, 414; *A.*, ii, 451.

[58] C. T. Hirst and J. E. Greaves, *Soil Sci.*, 1920, **9**, 41; *A.*, ii, 384.

[59] *J. Biol. Chem.*, 1918, **36**, 351; *A.*, 1919, ii, 78; compare *Ann. Reports*, 1919, **16**, 142.

magnesium carbonate, whilst in other cases Van Slyke's gasometric method [60] gives more accurate results.[61]

A method for the approximate estimation of phytin in plant extracts has been based on its precipitation in the presence of inorganic phosphates by an acetic acid solution of copper acetate of definite concentration, but the amounts of phytin precipitated vary with the nature of the plant.[62]

Organic Analysis.

Qualitative.—Formaldehyde gives colorations, which are not always distinctive of the aldehyde, with certain aromatic compounds, such as pyrogallol, β-naphthol, and salicylic acid, and these chromatic reactions may sometimes be used as tests of identity.[63] Another reagent which gives distinctive colorations with polyhydroxyphenols and other compounds of a phenolic character is sodium *p*-toluenedisulphochloroamide in neutral or alkaline solution, but the tests must be made under definite conditions as to the proportions of reacting substances and the temperature.[64]

Most of the tests for methyl alcohol are based on its conversion into formaldehyde, which is then identified either by chromatic reactions or by the formation of crystalline derivatives. These methods have been critically examined and their relative trustworthiness determined. Of the direct tests, all of which require a considerable proportion of methyl alcohol, that of Vivario,[65] in which the methyl alcohol is converted into potassium cyanide, gives very good results.[66]

A test to distinguish between methyl and ethyl alcohols has been based on the solubility of crystallised copper sulphate in the former,[67] but is untrustworthy in the case of mixtures of the dilute alcohols.[68] Lieben's reaction for iodoform has been modified so as to afford a sensitive test for traces of ethyl alcohol.[69]

A specific reaction for acetoacetic acid and its esters has been

[60] *J. Biol. Chem.*, 1917, **30**, 347; *A.*, 1917, ii, 422.

[61] C. S. Robinson, *Soil Sci.*, 1920, **10**, 41; *A.*, ii, 635.

[62] A. Rippel, *Biochem. Zeitsch.*, 1920, **103**, 163; *A.*, ii, 518.

[63] A. Rossi, *Boll. Chim. farm.*, 1919, **58**, 265; *A.*, ii, 63.

[64] A. Berthelot and M. Michel, *Bull. Sci. Pharmacol.*, 1919, **26**, 401; *A.*, ii, 336.

[65] *J. Pharm. Chim.*, 1914, [vii], **10**, 145; *A.*, 1914, ii, 780.

[66] A. O. Gettler, *J. Biol. Chem.*, 1920, **42**, 311; *A.*, ii, 562.

[67] Pannwitz, *Pharm. Zentr.-h.*, 1919, **60**, 441; *A.*, ii, 62.

[68] T. Sabalitschka, *ibid.*, 1920, **61**, 78; *A.*, ii, 271.

[69] R. Kunz, *Zeitsch. anal. Chem.*, 1920, **59**, 302; *A.*, ii, 711.

based on its condensation in hydrochloric acid solution to form β-methylumbelliferone, which in alkaline solution shows an intense blue fluorescence.[70]

From a study of various reactions for the identification of traces of hydrocyanic acid, the conclusion has been drawn that the ferro-cyanide test is the most characteristic.[71] The Prussian-blue test gives a reaction at a dilution of about $1:17 \times 10^4$ with hydrocyanic acid, whilst the Schönbein test, which is not distinctive, gives a reaction at $1:43 \times 10^6$ in the light and at $1:55 \times 10^6$ in the dark.[72] A test paper impregnated with a solution of *o*-tolidine, copper acetate, and dilute acetic acid is capable of detecting one part of hydrocyanic acid in two million parts of air.[73]

In the colour reaction with manganese salts for oxalates,[74] sufficient oxidation is produced by agitating the hot solution with a little alkali hydroxide.[75] Oxalic acid may be distinguished from tartaric and lactic acids by giving a violet coloration when heated with sulphuric acid and resorcinol.[76] If the test be applied as a zone reaction, a blue ring is formed at the junction of the liquids.[77]

A biochemical method of detecting dextrose in the presence of other sugars, such as mannose, lævulose, or arabinose, has been based on its conversion, in 70 per cent. methyl alcohol solution, by emulsin into β-methylglucoside, which may be identified in crystalline form.[78] Of various tests recommended for the detection of dextrose in urine, Fehling's test is the most sensitive, being capable of detecting 0·00125 per cent.[79] Traces of acetylmethyl-carbinol formed in the butylene-glycollic fermentation of sugars may be identified by oxidising the carbinol to diacetyl, which is then distilled, and identified by precipitation as nickel dimethyl-glyoxime.[80]

A very sensitive test for benzoic acid or for substances such as cocaine, which contain a benzoyl group, or which, like atropine, yield benzoic acid on oxidation, has been based on the diazotisa-tion of the aminobenzoic acids produced on nitration and reduc-

[70] V. Arreguine and E. D. Garcia, *Ann. Chim. anal.*, 1920, [ii], 2, 36 ; *A.*, ii, 273.   [71] L. Chelle, *ibid.*, 21 ; *A.*, ii, 202.

[72] J. B. Ekeley and I. C. Macy, *Proc. Colorado Sci. Soc.*, 1919, 11, 269; *A.*, ii, 202.

[73] J. Moir, *J. S. African Assoc. Anal. Chem.*, 1920, 3, 16 ; *A.*, ii, 715.

[74] V. Macri, *Boll. chim. farm.*, 1917, 56, 377 ; *A.*, 1917, ii, 511.

[75] H. Caron and D. Raquet, *Ann. Chim. anal.*, 1919, [ii], 1, 205 ; *A.*, 1919, ii, 438.

[76] K. Brauer, *Chem. Zeit.*, 1920, 44, 494 ; *A.*, ii, 517.

[77] L. H. Chernoff, *J. Amer. Chem. Soc.*, 1920, 42, 1784 ; *A.*, ii, 712.

[78] E. Bourquelot and M. Bridel, *Compt. rend.*, 1920, 170, 631 ; *A.*, ii, 337.

[79] G. E. Ewe, *Amer. J. Pharm.*, 1919, 91, 717 ; *A.*, ii, 132.

[80] M. Lemoigne, *Compt. rend.*, 1920, 170, 131 ; *A.*, ii, 198.

tion, and the formation of an orange-red precipitate on treating the diazo-compounds with an ammoniacal solution of β-naphthol.[81]

The behaviour of guaiacol with an oxydase affords a means of distinguishing it from creosote, the former giving a yellow coloration immediately, whilst the latter is colourless at first and then shows a slight violet tint.[82]

A new colour reaction for quinine, which takes place on the addition of pyridine in the presence of chlorine water, distinguishes the alkaloid from quinidine and euquinidine. The colour changes from yellow to rose, and finally to purplish-red.[83]

A sensitive and characteristic test for strychnine consists in treatment of the alkaloid salt solution with hydrochloric acid and zinc amalgam, and finally with potassium ferricyanide. In the presence of quantities down to 0·001 milligram of strychnine, a pink to rose-red coloration is obtained.[83] Various colour reactions of emetine have also been described.[84]

Pyrrole reacts with *p*-dimethylaminobenzaldehyde in an analogous manner to indole, and this must be borne in mind when applying Ehrlich's test.[85]

Quantitative.—A new form of absorption apparatus for elementary analysis has been devised, in which the carbon dioxide is absorbed by potassium hydroxide solution, and special precautions are used in drying the gas.[86] Certain organic substances, such as methyl esters and chloro-compounds, may be quantitatively oxidised by means of a mixture of sulphuric and chromic acids, the chlorine in the latter compounds being retained by an amalgamated copper spiral preceding the burette in which the carbon dioxide is measured.[87] Another new method of estimating carbon and hydrogen in organic compounds is based on their combustion in contact with platinum and cerium dioxide.[88]

Fusion with an alkaline mixture containing alkali nitrates, precipitation of the carbonate as calcium carbonate from a solution of the fused mass, and titration of the washed precipitate with hydrochloric acid, has been recommended for the estimation of carbon.[89]

A simple and rapid method of estimating halogens in organic compounds is to volatilise the substance with air through a quartz

[81] M. Guerbet, *Compt. rend.*, 1920, **171**, 40 ; *A.*, ii, 517.

[82] D. Ganassini, *Arch. ital. biol*, 1919, **69**, 73 ; *A.*, ii, 339.

[83] H. E. Buc, *J. Assoc. Off. Agric. Chem.*, 1919, **3**, 193 ; *A.*, ii, 397.

[84] A. Lahille, *Arch. méd. exp.*, **27**, 336 ; *A.*, ii, 134.

[85] E. Salkowski, *Biochem. Zeitsch.*, 1920, **103**, 185 ; *A.*, ii, 566.

[86] F. Friedrichs, *Zeitsch. angew. Chem.*, 1919, **32**, 388 ; *A.*, ii, 192.

[87] J. Guyot and L. J. Simon, *Compt. rend.*, 1920, **170**, 734 ; *A.*, ii, 332.

[88] K. Sumikura, *J. Tokyo Chem. Soc.*, 1919, **40**, 593 ; *A.*, ii, 126.

[89] L. Lescœur, *J. Pharm. Chim.*, 1920, [vii], **21**, 257 ; *A.*, ii, 332.

tube heated at 900—1000°, to absorb the products of combustion in sodium hydroxide solution containing sodium sulphite, and, after oxidising the excess of the latter with potassium permanganate, to estimate the halogen by Volhard's process.[90]

In using Kjeldahl's process for the estimation of nitrogen in aromatic nitro-compounds, it should be noted that accurate results may be obtained with ortho-compounds, but that those given by meta- and para-derivatives will be much too low.[91]

Estimation of nitro-groups by reduction with stannous chloride and titration of the excess of the reagent with iodine gives too low results with mononitrotoluenes, owing to the formation of p-chlorotoluidines, whilst the use of titanous chloride gives results about 3 per cent. too low in the case of o-nitrotoluene.[92] The low results given by a-nitronaphthalene and similar compounds may be obviated by substituting titanous sulphate for titanous chloride, and thus preventing chlorination.[93] Diazo-compounds, such as benzenediazonium chloride, may be titrated in hydrochloric acid solution by means of titanous chloride, with suitable indicators.[94]

A method for the estimation of methyl alcohol has been based on its oxidation with sulphuric acid and potassium dichromate, and gravimetric estimation of the carbon dioxide produced or volumetric estimation of the excess of dichromate.[95] In another method, the methyl alcohol is oxidised by means of ammonium persulphate, and the resulting formaldehyde estimated colorimetrically.[96]

For the estimation of ethylene glycol, oxidation with potassium dichromate and sulphuric acid, as in glycerol analysis, gives trustworthy results, but the acetin method is not applicable to dilute solutions of the glycol.[97]

An apparatus for estimating the carbon dioxide formed in the fermentation of sugars has been devised, and the method has been shown to be applicable to the differentiation of yeasts and enzymes by fermentation with appropriate sugars.[98]

[90] W. A. van Winkle and G. McP. Smith, J. Amer. Chem. Soc., 1920, 42, 333; A., ii, 328.

[91] B. M. Margosches and E. Vogel, Ber., 1919, 52, [B], 1992; A., ii, 50.

[92] D. Florentin and H. Vandenberghe, Bull. Soc. chim., 1920, [iv], 27, 158; A., ii, 271.

[93] T. Callan, J. A. R. Henderson, and Strafford, J. Soc. Chem. Ind., 1920, 39, 86T; A., ii, 331.

[94] E. Knecht and L. Thompson, J. Soc. Dyers and Col., 1920, 36, 215; A., ii, 647.

[95] A. Heiduschka and L. Wolff, Pharm. Zentr.-h., 1920, 61, 361; A., ii, 515.

[96] S. B. Schryver and C. C. Wood, Analyst, 1920, 45, 164; A., ii, 393.

[97] B. Müller, Chem. Zeit., 1920, 44, 513; A., ii, 515.

[98] A. Slator, J. Soc. Chem. Ind., 1920, 39, 149T; A., ii, 448.

Sucrose may be accurately estimated by a cryoscopic method.[99] For the estimation of sugars by inversion, chemical catalysts, such as benzenesulphonic acid, have advantages over enzymes.[1] The optical rotation of lævulose is destroyed by heating the sugar for seven hours with dilute hydrochloric acid, whereas that of dextrose is not affected. This has been made the basis of a method of estimating these sugars.[2] In the case of fruit juices, however, the most trustworthy method is to calculate the proportions of the respective sugars from the cupric-reducing power and the iodine value, the latter being characteristic for each sugar.[3] Another method of estimating dextrose has been based on the action of potassium cyanide for two days at 20°, and estimation of the excess of the reagent, or measurement in the change in rotation of the dextrose.[4]

A modification of the phenylhydrazine method for estimating pentosans consists in distilling the substance with sulphuric acid and estimating the furfuraldehyde by precipitation as hydrazone, and determination of the excess of phenylhydrazine in the filtrate.[5]

The coloration given by phenol when heated with Millon's reagent and nitric acid affords a means for its colorimetric estimation in the presence of other phenols.[6] Another method of estimating phenol is based on its titration with a solution of a diazonium compound, hydroxyazo-compounds being formed in the reaction.[7]

The conditions under which phenolphthalein combines quantitatively with iodine to form tetraiodophenolphthalein have been investigated, and a gravimetric method based on them.[8]

Silico- and phospho-tungstic acids are suitable reagents for the gravimetric and volumetric estimation of alkaloids under specified conditions, phosphotungstic acid being preferable in the case of aconitine and nicotine.[9] For the quantitative separation of strychnine from quinine, advantage has been taken of the fact that the former is only very slightly soluble in ethyl ether, and is left

[99] H. H. Dixon and T. G. Mason, *Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 1; *A.*, ii, 395.

[1] E. Hildt, *Ann. Chim. anal.*, 1920, [ii], **2**, 103 : *A.*, ii, 395.

[2] F. Lucius, *Zeitsch. Nahr. Genussm.*, 1919, **38**, 177 ; *A.*, ii, 132.

[3] (Miss) H. M. Judd, *Biochem. J.*, 1920, **14**, 255 ; *A.*, ii, 395.

[4] J. Bougault and J. Perrier, *Compt. rend.*, 1920, **170**, 1395 ; *A.*, ii, 452.

[5] P. Menaul and C. T. Dowell, *J. Ind. Eng. Chem.*, 1919, **11**, 1024 ; *A.*, ii, 209.

[6] R. M. Chapin, *ibid.*, 1920, **12**, 771 ; *A.*, ii, 645.

[7] R. M. Chapin, *ibid.*, 568 ; *A.*, ii, 563.

[8] S. Palkin, *ibid.*, 1920, **12**, 766 ; *A.*, ii, 643.

[9] A. Heiduschka and L. Wolff, *Schweiz-Apoth. Zeit.*, 1920, **58**, 213, 229 ; *A.*, ii, 780.

in the aqueous solution on extraction with ether in the presence of ammonia.[10] Reference may also be made to a method of estimating codeine by treatment of the plant extract with calcium hydroxide, and extraction of the filtrate with toluene.[11]

Tyrosine cannot be estimated quantitatively in the products of the hydrolytes of proteins by the method of Folin and Denis,[12] since the blue coloration is also given by tryptophan and other compounds in the mixture.[13]

It has been shown that the growth of yeast cells under specified conditions depends on the amount of so-called vitamins present, and a gravimetric method of estimating vitamins has been based on this fact.[14] The method has been found applicable to the estimation of the vitamin in food.[15] On the other hand, the results of other experiments have indicated that the test is influenced by so many factors as to have little, if any, value.[16]

Inorganic Analysis.

Qualitative.—Sodium alizarinsulphonate has been proposed as a sensitive indicator for the titration of mineral acids, and has the further advantage that it can be used both with ammonia and phosphoric acid.[17]

Several new schemes for the separation of cations into groups have been published. These include a modification of Petersen's method[18] of separating the cations of the third and fourth groups,[19] and a new method for the separation of various metals in the presence of phosphoric acid.[20] The use of thioacetic acid has been shown to offer several advantages over hydrogen sulphide as a reagent for the precipitation of the cations of Group II.[21]

Sensitive tests for manganic, ceric, cobaltic, and thallic compounds have been based on the fact that they give intense blue colorations with benzidine and other diphenyl derivatives.[22]

[10] A. R. Bliss, *J. Amer. Pharm. Assoc.*, 1919, **8**, 804; *A.*, ii, 276.

[11] H. E. Annett and H. Sen, *Analyst*, 1920, **45**, 321; *A.*, ii, 644.

[12] *J. Biol. Chem.*, 1912, **12**, 245; *A.*, 1912, ii, 1012.

[13] R. A. Gortner and G. E. Holm, *J. Amer. Chem. Soc.*, 1920, **42**, 1678; *A.*, ii, 643.

[14] R. J. Williams, *J. Biol. Chem.*, 1920, **42**, 259; *A.*, ii, 648.

[15] W. H. Eddy and H. C. Stevenson, *ibid.*, 1920, **43**, 295; *A.*, ii, 716.

[16] G. de P. Souza and E. V. McCollum, *ibid.*, 1920, **44**, 113; *A.*, i, 919.

[17] W. Mestrezat, *J. Pharm. Chim.*, 1920, [vii], **21**, 185; *A.*, ii, 263.

[18] *Zeitsch. anorg. Chem.*, 1910, **67**, 253; *A.*, 1910, ii, 654.

[19] P. de Pauw, *Chem. Weekblad*, 1920, **17**, 191; *A.*, ii, 451.

[20] H. Remy, *Zeitsch. anal. Chem.*, 1919, **58**, 385; *A.*, ii, 186.

[21] N. Alvarez, *Bol. minero soc. nac. min. Chile*, 1919, **31**, 181; *A.*, ii, 381.

[22] F. Feigl, *Chem. Zeit.*, 1920, **44**, 689; *A.*, ii, 710.

Turning to the specific tests for individual substances, it has been shown that iodic acid may be used as a distinctive microscopical reagent for the detection of ammonia, characteristic crystals of ammonium iodate being formed.[23]

The differences between the deposits formed by hydrogen arsenide, cacodylic acid, methylarsinic acid, and neosalvarsan in Marsh's test have been studied, and it has been found that the addition of platinum chloride to promote the evolution of hydrogen may fix some of the arsenic in the flask.[24] The best method of detecting arsenic in sulphur is by oxidation with bromine and nitric acid, and application of Gutzeit's test to the product.[25] A test for salts of tin has been based on the insolubility of stannous or stannic iodide in sulphuric acid. The yellow precipitate may be distinguished from the similar compound formed by arsenic by the fact that it is soluble in dilute hydrochloric acid. The corresponding antimony salt is brick-red and flocculent.[26] A distinctive test for osmium tetroxide is afforded by the blue coloration which it gives with pyrogallol, whilst the vapour may be identified by giving a permanent stain, due to the reduced osmium, with a slightly greasy finger-print.[27]

Xanthic acid may be used as a distinctive reagent for molybdenum,[28] but it is essential that oxalates should not be present, whilst copper, cobalt, nickel, iron, and uranium interfere with the test.[29]

For the detection of traces of cobalt, the coloration given by β-nitroso-α-naphthol is much more sensitive than that obtained with α-nitroso-β-naphthol.[30] Cobalt may be detected in the presence of nickel by means of potassium xanthate. The xanthates of both metals are precipitates, but the cobalt compound is insoluble in ammonia, whereas the nickel compound dissolves, forming a blue solution.[31]

Most cerous and ceric compounds give a bright blue coloration when moistened with a solution of benzidine in acetic acid, and the reaction may be used for detecting cerium in the presence of other metals of the ammonium sulphide group of rare earths, with the exception of thallium.[32]

[23] G. Denigès, Compt. rend., 1920, 171. 177; A., ii, 555.

[24] D. Ganassini, Boll. Chim. farm., 1919, 58, 385; A., ii, 51.

[25] H. S. Davis and M. D. Davis, J. Ind. Eng. Chem., 1920, 12, 479; A., ii, 148.　　[26] A. Mazuir, Ann. Chim. anal., 1919, [ii], 2, 9; A., ii, 197.

[27] C. A. Mitchell, Analyst, 1920, 45, 125; A., ii, 335.

[28] S. L. Malowan, Zeitsch. anorg. Chem., 1919, 108, 73; A., ii, 59.

[29] J. Koppel, Chem. Zeit., 1919, 43, 777; A., ii, 58.

[30] I. Bellucci, Gazzetta, 1919, 49, ii, 294; A., ii, 194.

[31] L. Compin, Ann. Chim. anal., 1920, [ii], 2, 218; A., ii, 559.

[32] F. Feigl, Oesterr. Chem. Zeit., [ii], 22, 124; A., ii, 54.

Iodic acid has been found to be a useful microchemical reagent for calcium, strontium, or barium, the distinctive forms of the crystalline iodates being observed.[33] It may also be used to distinguish between the salts of barium and radium.[34]

For the detection of magnesium, advantage has been taken of the fact that it gives a bluish-violet coloration with an alcoholic solution of alkannin, the similar colorations given by strontium and manganese being distinguished by their behaviour after acidification.[35]

The applicability and sensitiveness of various reactions for potassium have been determined, and the most sensitive reagent has been found to be sodium–bismuth thiosulphate, which is capable of detecting 1 part in 57,000.[36]

The colour changes which take place in the diphenylamine reaction for nitrates have been studied, and a sensitive modification of the reagent devised for microchemical tests.[37] A blue coloration may be produced in the diphenylamine reagent by the presence of ferric salts in the sulphuric acid.   To prevent this, such acid should be boiled, and cooled to reduce the ferric salts.[38]

A sensitive test for nitrites in the presence of nitrates is the production of a red coloration on treating the solution successively with acetic acid, potassium oxalate solution, manganous sulphate, and hydrogen peroxide.[39] For the detection of phosphates in the presence of barium, a modification of Denigès' strychnine–molybdate reagent is sensitive, but must be freshly prepared.[40]

Quantitative.—It is in this branch of the subject that the greatest activity has been shown, and the contributions to different journals have been so numerous that it has been necessary to select only the more important for mention in this Report.

A method of using potassium chlorate as an original standard for the titration of alkali has been described. The chlorate is reduced by means of sulphur dioxide, the excess of the latter removed, and the sulphuric acid formed in the reduction titrated with alkali—$KClO_3 + 3SO_2 + 3H_2O = 3H_2SO_4 + KCl$.[41] Another suitable standard is potassium hydrogen phthalate, which contains

[33] G. Denigès, *Compt. rend.*, 1920, **170**, 996 ; *A.*, ii, 388.

[34] G. Denigès, *ibid.*, 1920, **171**, 633 ; *A.*, ii, 706.

[35] F. Eisenlohr, *Ber.*, 1920, **53**, [B] 1476 ; *A.*, ii, 708.

[36] O. Lutz, *Zeitsch. anal. Chem.*, 1920, **59**, 145 ; *A.*, ii, 509.

[37] E. M. Harvey, *J. Amer. Chem. Soc.*, 1920, **42**, 1245 ; *A.*, ii, 504.

[38] F. Haun, *Zeitsch. Nahr. Genussm.*, 1920, **39**, 355 ; *A.*, ii, 555.

[39] P. H. Hermans, *Pharm. Weekblad*, 1920, **57**, 462 ; *A.*, ii, 448.

[40] L. Débourdeaux, *Bull. Sci. pharmacol.*, 1920, **27**, 70 ; *A.*, ii, 505.

[41] H. B. van Valkenburgh, *J. Amer. Chem. Soc.*, 1920, **42**, 757 ; *A.*, ii, 387.

no water of crystallisation and is not hygroscopic.[42] In preparing the salt, it is advisable to crystallise it above 20°, to prevent the formation of a more acid salt.[43] A useful indicator for coloured liquids has been found in ferrous sulphide, the formation of which is prevented by a slight trace of acid. A crystal of pure ferrous ammonium sulphate is added to the solution, which is then treated with hydrogen sulphide, and titrated with alkali until a permanent black coloration is obtained.[44]

Various experiments have been made with salts of magnesium, zinc, mercury, and aluminium to determine the degree of accuracy obtainable in the acidimetric titration of the salts of heavy metals which form insoluble hydroxides.[45]

In the volumetric estimation of sulphates by oxidation of benzidine sulphate with potassium permanganate,[46] it is essential that the solution from which the benzidine sulphate is precipitated should be free from organic matter, iron, heavy metals, nitrates, and phosphates.[47]

A new volumetric reduction method with arsenic trioxide has been devised, in which an oxidising agent, such as a chlorate or chromate, is treated with excess of arsenic trioxide in the presence of hydrochloric acid, and the solution subsequently titrated with potassium bromate solution.[48]

Several new iodometric methods have been published. The conditions for the iodometric estimation of acids, more especially weak acids, have been investigated, and the applicability of various methods has been determined.[49] The direct estimation of chloric acid in a strongly acid medium gives too high results, owing to oxidation of hydrogen iodide, but Rupp's method[50] is trustworthy.[51] For the iodometric estimation of arsenic acid, the reacting mixture should be heated to 100° and contain specified proportions of potassium iodide and hydrogen chloride.[52]

Stannous tin may be more accurately estimated by a volumetric method in an acid solution. Titration with standard iodine solu-

[42] W. S. Hendrixson, *J. Amer. Chem. Soc.*, 1920, **42**, 724; *A.*, ii, 382.

[43] F. D. Dodge, *ibid.*, 1655; *A.*, ii, 628.

[44] J. Houben, *Ber.*, 1919, [B], 1613; *A.*, ii, 53.

[45] I. M. Kolthoff, *Zeitsch. anorg. Chem.*, 1920, **112**, 172; *A.*, ii, 709.

[46] G. W. Raiziss and H. Dubin, *J. Biol. Chem.*, 1914, **18**, 297; *A.*, 1914, ii, 671.

[47] B. L. Hibbard, *Soil Sci.*, 1919, **8**, 61; *A.*, ii, 191.

[48] F. de Bacho, *Annali Chim. Appl.*, 1919, **12**, 153; *A.*, ii, 188.

[49] I. M. Kolthoff, *Pharm. Weekblad*, 1920, **57**, 53; *A.*, ii, 121.

[50] E. Rupp, *Zeitsch. anal. Chem.*, 1917, **56**, 580; *A.*, 1918, ii, 125.

[51] I. M. Kolthoff, *Pharm. Weekblad*, 1919, **56**, 460; *A.*, ii, 190.

[52] P. Fleury, *J. Pharm. Chim.*, 1920, [vii], **21**, 385; *A.*, ii, 448.

tion in the presence of hydrochloric acid is satisfactory in the case of many compounds.[53] The iodometric estimation of chromium gives too high results, owing to the influence of atmospheric oxygen on the reaction.[54]

To obtain accurate results in the iodometric estimation of potassium ferricyanide, the acid concentration must be kept sufficiently high and the time of the reaction restricted.[55]

A new volumetric method of estimating nickel has been based on the titration of the acid which is liberated in the reaction with dimethylglyoxime.[56]

Further work on the use of organic solvents for the quantitative separation of metals has shown that the method of progressive precipitation previously described [57] is suitable for the separation of magnesium from sodium and potassium, the salts of the latter metals being precipitated first by means of alcohol and ether.[58]

New applications of the use of cupferron (the ammonium salt of nitrosophenylhydroxylamine) have been published. The reagent gives good results in the estimation of iron, copper, titanium, zirconium, thorium, and vanadium in the absence of certain interfering substances, but in many cases offers no advantage over previous methods.[59] It is most serviceable for the separation of copper from arsenic, and especially from antimony. Like a-nitroso-β-naphthol, it is a useful reagent for separating elements into groups.[60] In neutral solution it gives precipitates with all metals except the alkali metals, and the precipitates may be separated into two groups by their behaviour towards chloroform and dilute acids.[61] If corrections for the solubility of the precipitate be applied, iron may be accurately separated from manganese by cupferron.[62] A trustworthy method has also been worked out for the use of the reagent in the separation of tin and antimony.[63]

A simple method of estimating mercury is to cause it to be

[53] J. G. F. Druce, *Chem. News*, 1920, **121**, 173 ; *A.*, ii, 710.

[54] O. Meindl, *Zeitsch. anal. Chem.*, 1919, **58**, 529 ; *A.*, ii, 390.

[55] I. M. Kolthoff, *Pharm. Weekblad*, 1919, **56**, 1618 ; *A.*, ii, 67.

[56] J. Holluta, *Monatsh.*, 1919, **40**, 281 ; *A.*, ii, 57.

[57] S. Palkin, *J. Amer. Chem. Soc.*, 1916, **38**, 2326 ; *A.*, 1917, ii, 43.

[58] *Ibid.*, 1920, **42**, 1618 ; *A.*, ii, 637.

[59] G. E. F. Lundell and H. B. Knowles, *J. Ind. Eng. Chem.*, 1920, **12**, 344 ; *A.*, ii, 390.

[60] I. Bellucci and A. Chiucini, *Gazzetta*, 1919, **49**, ii, 187 ; *A.*, ii, 54.

[61] V. Auger, *Compt. rend.*, 1920, **170**, 995 ; *A.*, ii, 391.

[62] E. H. Archibald and R. V. Fulton, *Trans. Roy. Soc. Canada*, 1919, **13**, [iii], 243 ; *A.*, ii, 512.

[63] A. Kling and A. Lassieur, *Compt. rend.*, 1920, **170**, 1112 ; *A.*, ii, 452.

deposited on a coil of copper gauze, and to estimate the amount of the deposit by the loss in weight after heating the coil in a current of hydrogen.[64]

Arsenic may be separated from antimony, tin, copper, lead, mercury, and iron by a modification of the distillation method, whilst antimony may be separated from tin by volatilising antimony chloride at 155—165° from solutions to which phosphoric acid has been added to render the tin non-volatile.[65] A modification of the Marsh-Berzelius test has been described in which the hydrogen arsenide is conducted over red-hot copper, which retains the arsenic as arsenides. The results are about 1·4% too low, possibly owing to retention of arsenic in the flask in the form of a stable complex.[66]

In order to obtain a precipitate of secondary zirconium phosphate of constant composition in the precipitation of zirconium by the phosphate method, the solution should contain from 2 to 20 per cent. of sulphuric acid, and an excess of diammonium hydrogen phosphate ten to one hundred times in excess of the theoretical quantity should be added.[67] A new method, applicable to zirconia ores, is to precipitate the zirconium with selenious acid, and to ignite the basic selenite, which leaves a residue of zirconia.[68]

The difficulty of precipitating molybdenum quantitatively as sulphide may be obviated by having a sufficient quantity of formic acid in the solution, and seeing that the whole of the molybdenum is present as molybdate.[69]

From a study of various methods of estimating uranium, the conclusion has been drawn that precipitation with ammonium sulphide or with ammonia gives the most trustworthy results. In either case, the precipitate leaves uranoso-uranic oxide on ignition.[70] Precipitation of uranium as uranyl ammonium phosphate is also a good method, but has the drawback that the ignited uranyl pyrophosphate rapidly absorbs moisture.[71] For the estimation of minute quantities of uranium, a colorimetric method has been based on the red coloration given by uranyl salts with sodium salicylate.[72]

[64] H. B. Gordon, *Analyst*, 1920, **45**, 41 ; *A.*, ii, 194.

[65] W. Strecker and A. Riedemann, *Ber.*, 1919, **52**, [B], 1935 ; *A.*, ii, 51.

[66] B. S. Evans, *Analyst*, 1920, **45**, 8 ; *A.*, ii, 125.

[67] G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1919, **41**, 1801 ; *A.*, ii, 60.

[68] M. S. Smith and C. James, *ibid.*, 1920, **42**, 1764 ; *A.*, ii, 710.

[69] J. Štěrba-Böhm and J. Vostřebal, *Zeitsch. anorg. Chem.*, 1920, **110**, 81 ; *A.*, ii, 335.   [70] R. Schwarz, *Helv. Chim. Acta*, 1920, **3**, 330 ; *A.*, ii, 391.

[71] C. A. Pierre, *J. Ind. Eng. Chem.*, 1920, **12**, 60 ; *A.*, ii, 197.

[72] Müller, *Chem. Zeit.*, 1919, **43**, 739 ; *A.*, ii, 60.

The perchlorate method for the estimation of potassium gives accurate results under specified conditions.[73] The method previously described[74] is rendered more trustworthy by extracting the sodium perchlorate with alcohol containing perchloric acid, instead of with a saturated solution of potassium perchlorate.[75] By using aniline perchlorate in place of perchloric acid, the process is rendered more rapid than any other method of estimating potassium.[76] The proportion of potassium in the mixed precipitate of potassium and sodium cobaltinitrite may be calculated from a gravimetric or electrolytic estimation of the cobalt.[77] Another method of estimating the proportions of the two metals in mixtures of the salts is to convert them into nitrates and determine the melting points.[78]

Chromic acid liberates bromine quantitatively from bromides at the ordinary temperature, and the bromine may be removed by aspiration, whereas chlorides under the same conditions yield only traces of chlorine. A method of estimating bromine in mineral waters has been based on these facts.[79]

The conditions for effecting the quantitative estimation of phosphoric acid by precipitating and weighing it as ammonium phosphomolybdate have been investigated, and a trustworthy method devised. For the nephelometric estimation of traces of phosphoric acid, the use of a reagent prepared by the interaction of strychnine sulphate and sodium molybdate gives excellent results.[80]

Electrochemical Analysis.

There have been relatively few contributions to gravimetric electrolytic methods of analysis, but much work has been done in connexion with the investigation of methods of electrometric titration and their extension to further substances.

It has been shown that in many cases the end-point of a titration is sharply indicated by measurement of the terminal voltage between two electrodes, one of which is immersed in the solution

[73] R. L. Morris, *Analyst*, 1920, **45**, 349; *A.*, ii, 707.

[74] G. P. Baxter and M. Kobayashi, *J. Amer. Chem. Soc.*, 1917, **39**, 249; *A.*, 1917, ii, 270.

[75] G. P. Baxter and M. Kobayashi, *ibid.*, 1920, **42**, 735; *A.*, ii, 388.

[76] S. B. Kuzirian, *Proc. Iowa. Acad. Sci.*, 1917, **24**, 547; *A.*, ii, 450.

[77] P. Wenger and C. Hémen, *Ann. Chim. anal.*, 1920, [ii], **2**, 198; *A.*, ii, 556.

[78] A. Quartaroli, *Gazzetta*, 1920, **50**, ii, 64; *A.*, ii, 635.

[79] W. F. Baughman and W. W. Skinner, *J. Ind. Eng. Chem.*, 1919, **11**, 954; *A.*, ii, 48.

[80] H. Kleinmann, *Biochem. Zeitsch.*, 1919, **99**, 150; *A.*, ii, 634.

under examination, and is capable of yielding the same ions to the solution, whilst the second, or comparison electrode, is composed of the same metal as the first and of the precipitate or other product of the reaction. Owing to the slow action of the electrode, the method does not give sharp results in the titration of hydrogen-ion concentration.[81] A hydrogen electrode giving a sharp end-point in acidimetric titrations has been described, and shown to be suitable for the estimation of strong acids in the presence of weak acids.[82] Other electrometric methods may be used for the estimation of weak acids, such as acetic acid, in the presence of strong acids, such as hydrochloric acid.[83] A simple method of acidimetric or alkalimetric titration is to connect the solution to be titrated with another of known P_H value, each being provided with a hydrogen electrode, and to continue the titration until the same hydrogen-ion concentration is shown by both solutions.[84] Carbonic acid and its salts in dilute solution can be titrated in this way,[85] whilst phosphoric acid in dilute solution behaves like a mono- or di-basic acid, the first end-point being sharp, whilst the second is less distinct.[86]

A method for the electrometric estimation of arsenic in coloured solution is to titrate arsenic trioxide with iodine solution in the presence of sodium hydrogen carbonate, and to titrate arsenic pentoxide in sulphuric acid solution at 95° with sodium iodide solution.[87] Lead and zinc salts may be accurately titrated with potassium ferrocyanide, but in the case of other metals the precipitates are not constant in composition.[88]

The fact that mercuric acetate forms a stable, complex compound with allyl alcohol has been utilised for the electrometric titration of that alcohol by means of a standard solution of the mercury salt.[89]

The presence of soluble ferricyanides or chlorides in moderate proportion does not interfere with the titration of ferrocyanides with potassium permanganate solution, but salts yielding pre-

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[81] W. D. Treadwell and L. Weiss, *Helv. Chim. Acta*, 1919, **2**, 680; *A.*, ii, 119.

[82] W. D. Treadwell and L. Weiss, *ibid.*, 1920, **3**, 433; *A.*, ii, 553.

[83] I. M. Kolthoff, *Rec. trav. chim.*, 1920, **39**, 280; *A.*, ii, 327.

[84] P. E. Klopsteg, *Science*, 1920, **52**, 18; *A.*, ii, 700.

[85] I. M. Kolthoff, *Zeitsch. anorg. Chem.*, 1920, **112**, 155; *A.*, ii, 705.

[86] I. M. Kolthoff, *ibid.*, 165; *A.*, ii, 705.

[87] C. S. Robinson and O. B. Winter, *J. Ind. Eng. Chem.*, 1920, **12**, 775; *A.*, ii, 635.

[88] Erich Müller, *Zeitsch. angew. Chem.*, 1919, **32**, 351; *A.*, ii, 54.

[89] E. Biilmann, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, 1; *A.*, i, 131.

cipitates with either ferro- or ferri-cyanides must not be present.[90]

The alcoholic strength of beer or wine may be rapidly estimated by distillation with magnesium oxide (after removal of carbon dioxide), treatment of the distillate with oxalic acid solution, and determination of the specific conductivity of the mixture and of the original oxalic acid solution. The required result is then obtained by the use of a formula.[91]

Amino-acids may be estimated alkalimetrically by means of the hydrogen electrode, and a simple method for the purpose has been devised.[92] The conductometric process has also been adapted to the titration of phenols, cresols, and certain hydroxy-acids.[93] A similar process has been worked out for the estimation of alkaloids and their salts, the alkaloids themselves being titrated with acid, whilst alkaloid salts are titrated with alkali.[94]

An indirect method for the electrolytic estimation of halogens has been based on the fact that the solution can be electrolysed by means of a silver anode, with the formation of an adherent deposit on the anode, and without precipitation in the solution, provided that an anode potential of 0.59 volt is not exceeded.[95]

When an ammoniacal solution of nickel and a salt of arsenic acid is electrolysed, the nickel is quantitatively precipitated without any arsenic, whereas cobalt under the same conditions carries down a certain proportion of arsenic.[96]

Reference may also be made to methods in which rotating reductors are used in the estimation of iron[97] and of molybdenum.[98]

Water Analysis.

The principal contributions to the analysis of drinking-water have been in connexion with the dissolved carbon dioxide. It has been shown that the simple mass-law equation of the primary ionisation of carbonic acid enables the hydrogen-ion concentration of natural waters to be approximately calculated.[99]

In titrating the free carbon dioxide and that present as hydrogen

[90] G. L. Kelley and R. T. Bohn, J. Amer. Chem. Soc., 1919, 41, 1776; A., ii, 134.

[91] I. M. Kolthoff, Rec. trav. chim., 1920, 39, 126; A., ii, 198.

[92] E. L. Taube, J. Amer. Chem. Soc., 1920, 42, 174; A., ii, 396.

[93] I. M. Kolthoff, Zeitsch. anorg. Chem., 1920, 112, 187; A., ii, 711.

[94] I. M. Kolthoff, ibid., 196; A., ii, 781.

[95] J. H. Reedy, J. Amer. Chem. Soc., 1919, 41, 1898; A., ii, 122.

[96] N. H. Furman, ibid., 1920, 42, 1789; A., ii, 710.

[97] W. Scott, J. Ind. Eng. Chem., 1919, 11, 1135; A., ii, 128.

[98] W. Scott, ibid., 1920, 12, 578; A., ii, 578.

[99] R. E. Greenfield and G. C. Baker, ibid., 1920, 12, 989; A., ii, 771.

carbonate in moorland waters, errors are caused by the presence of weak organic acids which are simultaneously titrated. To determine the solvent action of such waters on limestone, the water is shaken at intervals with powdered marble in a closed flask, and a portion then titrated with $N/10$-acid. The difference between the result and that obtained without the addition of marble gives the amount of calcium carbonate dissolved.[1]

It has been shown by Tillmanns and Heublein[2] that the free carbon dioxide in soft water has a much greater solvent action on calcium carbonate than the same amount of carbon dioxide in hard water. In the case of waters containing iron hydrogen carbonate, the semi-combined and the combined carbon dioxide in the iron compound are titrated simultaneously with the free carbon dioxide, and, as a correction, 1·1 milligram of carbon dioxide must be deducted for each milligram of ferric oxide present.[3]

In using Escaïch's colour test for nitrites[4] in water, the results are uncertain in the presence of chlorides, which must therefore be removed by means of silver nitrate before applying the test.[5]

C. AINSWORTH MITCHELL.

[1] V. Rodt, *Chem. Zeit.*, 1920, **44**, 469; *A.*, ii, 507.
[2] *Gesundheits-Ing.*, 1912, **35**, 669; *A.*, 1913, ii, 51.
[3] H. Noll, *Zeitsch. angew. Chem.*, 1920, **33**, i, 182; *A.*, ii, 555.
[4] *J. Pharm. Chim.*, 1918, [vii], **17**, 395; *A.*, 1918, ii, 273.
[5] A. Escaïch, *ibid.*, 1920, [vii], **22**, 138; *A.*, ii, 644.

PHYSIOLOGICAL CHEMISTRY.

SINCE writing last year's Report the deaths of the following have occurred: G. von Bunge, Sir Thomas Fraser, Armand Gautier, Wilhelm Pfeffer, Max Siegfried, and Nathan Zuntz. Von Bunge was Professor of Physiological Chemistry at Basle, and the author of a well-known text-book. His best known research was concerned with the mineral constituents of blood and milk. Fraser was for many years professor of materia medica at Edinburgh; he introduced Calabar beans into medicine in the early sixties, but it is chiefly during the last decade that physostigmine has attracted much attention from organic chemists. A study of arrow poisons led him to the therapeutic application of strophanthin; he made also an extensive study of snake venoms, and his name is associated with that of Crum Brown in the generalisation that quaternary salts of organic bases have a curare-like action. Gautier, the veteran of French biochemistry, originally received a medical training, but became later assistant to Wurtz and was for many years Professor of Medical Chemistry at Paris. He is known for his studies on ptomaines and on the occurrence of the biologically rare elements (fluorine, arsenic, etc.). He also worked on arsenical drugs and questions of hygiene, food and general chemistry.

Pfeffer's "Osmotische Untersuchungen," published in 1877, became known five years later to Van't Hoff, through the latter's botanical colleague, de Vries, and thus became one of the most fruitful stimuli ever given by biology to physical science. Doubtless Pfeffer owed some of his success to his early training as a chemist; his doctor's dissertation related to an organic chemical problem. Siegfried also began as an organic chemist; as assistant to Drechsel he was diverted to physiological chemistry. He became extraordinary and (1919) ordinary professor of this subject at Leipzig. His best known work is on the extractives of muscle and the kyrines. Zuntz, on the other hand, was by training a physiologist, and an early appointment at the Agricultural College of Poppelsdorf, near Bonn, determined his career. He was mainly

concerned with nutrition and gaseous interchange, for which he worked out exact methods of gas analysis. At Berlin he would rejoice in later years in showing visitors his respiration chamber capable of accommodating an ox.

In July, 1920, an international congress of Physiology met at Paris; the next meeting is to take place at Edinburgh in 1922. In France the Société de Chimie Biologique, founded in 1914, has resumed the publication of its *Bulletin*. After two pre-war numbers, the third followed in October, 1919, and others during the present year. Besides original papers there have been occasional résumés of current questions, valuable on account of their lucidity. During the year a new periodical of biochemical interest has begun under the title of the *British Journal of Experimental Pathology*.

In America a series of monographs has now also been started, "on experimental biology and general physiology." Some of those announced are on more or less chemical subjects. In the series of "Monographien aus dem Gesamtgebiet der Physiologie der Pflanzen und der Tiere," there appeared last year "Die Narkose in ihrer Bedeutung für die allgemeine Physiologie," by H. Winterstein, and this year, "Die biogenen Amine," by M. Guggenheim. The latter is an excellent up-to-date account of the chemical and physiological properties of the simpler bases of biological interest, written by a well-known worker on the subject. The production of large hand-books has been resumed in Germany to some extent. A new "Handbuch der biologischen Arbeitsmethoden" is appearing under the general editorship of E. Abderhalden. It will replace the "Biochemische Arbeitsmethoden," now out of print, and is on a very extensive scale; there will be 13 parts, of which the first, dealing with purely chemical methods, is of primary interest to us here. By the publication, towards the end of 1920, of the second half of his "Lehrbuch der physiologischen Chemie," E. Abderhalden has completed the fourth edition. The first half appeared more than a year ago. The second half (which actually bears the date 1921) has been almost entirely rewritten. It is a few pages shorter than Vol. II. of the 1915 edition, in spite of a new chapter on vitamins. In 1920 there has also appeared Part II. of the first volume of a "Handbuch der experimentellen Pharmakologie," edited by A. Heffter. This, the first instalment of the whole work, deals with many important alkaloids, for example, cinchona alkaloids and derivatives, colchicine, cocaine, ipecacuanha alkaloids, strychnine. The manuscript was prepared before the war and although some articles have apparently been revised to 1918, others do not extend beyond 1913, and do not take into

account the therapeutic discoveries of the war. The book will, however, doubtless interest some chemists. Two outstanding French books on bacteriology should also be mentioned here, both the result of scientific isolation during the war: "Traité de l'immunité dans les maladies infectueuses," by J. Bordet, and "L'infection bacillaire et la tuberculose chez l'homme et chez les animaux," by A. Calmette. The former book especially should appeal to anyone seeking a chemical basis for immunological phenomena.

Metabolism of Carbohydrates.

The hypothesis of Chauveau, that fats only become a source of muscular energy after they have been transformed into carbo-hydrates, was shown to be untenable some twenty years ago by the work of Zuntz and his pupils, who drew the conclusion that fats and carbohydrates are isodynamic, that is, that in both these classes of foodstuffs the same fraction of the heat of combustion can be converted into work. The researches of Fletcher, Hopkins, A. V. Hill and others have, however, made it pretty certain that the process of muscular contraction is associated with chemical reactions of substances closely related to the carbohydrates, and then it becomes difficult to understand that the utilisation of fats is not attended by some loss of energy. These considerations have led A. Krogh and K. G. Lindhard [1] to an important reinvestigation of "the relative value of fat and carbohydrate as sources of muscu-lar energy." Their method involved the determination of the respiratory quotient of a subject working an ergometer in a respira-tion chamber, and they determined this quotient within 0·005 by very accurate analysis of the air passing through the chamber. In connexion with this A. Krogh has published subsidiary papers [2] on a gas analysis apparatus accurate to 0·001 per cent., and on the calibration, accuracy and use of gas meters, which papers may be of use to non-biological chemists. Krogh and Lindhard find that the net expenditure of energy (after deducting the standard meta-bolism) necessary to perform the equivalent of one calorie of technical work on the ergometer varied from 4–5·5 calories. In the three best series of experiments it was 4·6 cal. when fat alone was catabolised (R.Q. = 0·71) and 4·1 cal. for carbohydrate alone (R.Q. = 1·0). This shows a waste of energy from fat of 0·5 cal., or 11 per cent. of its heat of combustion. The authors suggest as a working hypothesis that both during rest and work the proportion of fat to carbohydrate katabolised is a function of the available

[1] Biochem. J., 1920, 14, 290 ; A., i, 692.
[2] Ibid., 267, 282 ; A., ii, 553, 630.

supply of these substances. With the respiratory quotient below 0·8 carbohydrate is formed from fat and provisionally stored; the reverse transformation takes place with a respiratory quotient above 0·9.

A novel aspect of the metabolism of reducing sugars is dealt with by J. A. Hewitt and J. Pryde,[3] who find that solutions of d glucose introduced into the intestine of the living animal undergo rapid downward mutarotation from +52·5° to below +19°, and in one experiment the solution even became lævorotatory. On withdrawal from the intestine the reverse change takes place more slowly, until the original rotation of a- and β-glucoses in equilibrium is reached. This change is not due to preferential absorption of the a-form or to disaccharide formation, but probably to the formation of γ-glucose in excess of any amount normally present in glucose solution which has reached an equilibrium.

Proteins.

Various classifications of proteins have been discussed by P. Thomas.[4] The two principal methods for determining the degree of hydrolysis of a protein are that of Van Slyke, who determines the free amino-groups, and that of Sörensen, who titrates the carboxyl groups. The former method has been elaborated into an indirect analysis of amino-acids in groups, of which the largest is that with amino-nitrogen, comprising glycine, alanine, serine, phenylalanine, tyrosine, valine, the three leucines, aspartic and glutamic acids. This large group A. C. Andersen[5] subdivides further by neutralising the solution with sodium hydroxide in the way indicated by Sörensen for his formol titration. Under these conditions only aspartic and glutamic acids combine with one equivalent of sodium hydroxide, and the monocarboxylic acids remain in the free state. On ashing such a solution the amount of sodium carbonate in the residue is equivalent to the monamino-dicarboxylic acids present.

Amino-Acids.

H. D. Dakin[6] has synthesised racemic β-hydroxyglutamic acid, of which an active modification was discovered by him in casein.[7] The synthesis presented unexpected difficulties and several attempted methods failed or gave only minute yields. The best

[3] Biochem. J., 1920, **14**, 395; A., i, 508.
[4] Bull. Soc. Chim. biol., 1920, **2**, 112; A., i, 644.
[5] Kong. Vet. og Landbohöjskole Aarskrift, 1917, 308; A., ii, 647.
[6] Biochem. J., 1919, **13**, 398; A., i, 294.
[7] Ann. Reports, 1919, **16**, 153; A., 1919, i, 150.

results were obtained by the following method. Glutamic acid was converted by potassium cyanate into α-carbamidoglutaric and then into hydantoinpropionic acid (I). The action of bromine on

$$
\begin{array}{cccc}
\left.\begin{array}{l} \text{CO-NH} \\ \text{CH·NH} \end{array}\right\rangle\text{CO} &
\left.\begin{array}{l} \text{CO-NH} \\ \text{CH·NH} \end{array}\right\rangle\text{CO} &
\left.\begin{array}{l} \text{CO-NH} \\ \text{CH·NH} \end{array}\right\rangle\text{CO} &
\begin{array}{l} \text{CO}_2\text{H} \\ \text{CH·NH}_2 \end{array} \\
\text{CH}_2 & \text{CHBr} & \text{CH} & \text{CH·OH} \\
\text{CH}_2 & \text{CH}_2 & \text{CH} & \text{CH}_2 \\
\text{CO}_2\text{H} & \text{CO}_2\text{H} & \text{CO}_2\text{H} & \text{CO}_2\text{H} \\
\text{(I.)} & \text{(II.)} & \text{(III.)} & \text{(IV.)}
\end{array}
$$
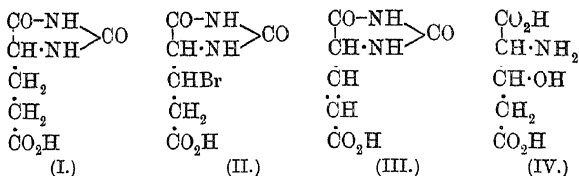
the latter is complex; after bromine enters the molecule it is split off again as hydrogen bromide, introducing a double bond in the βγ-position, but when the bromination is carried out in glacial acetic acid saturated with hydrogen bromide, the latter is added on again and *i*-hydantoin-β-bromopropionic acid (II) results. On boiling this with water hydantoinacrylic acid (III) is formed with the double bond in the required αβ-position. This acid is boiled with baryta solution until half the nitrogen has been evolved as ammonia, indicating the complete opening of the hydantoin ring. At the same time a molecule of water is added and inactive β-hydroxyglutamic acid (IV) results, in a yield of 20 per cent. of the hydantoinacrylic acid or 2 per cent. of the glutamic acid employed. The original paper should be consulted by organic chemists desirous of effecting a smoother synthesis. A secondary result of Dakin's experiments was the preparation of malic semi-aldehyde $CHO·CH(OH)·CH_2·CO_2H$, which, however, does not lend itself to the application of the Strecker synthesis.

Apart from casein Dakin has now also found his new amino-acid in glutenin (2·4 per cent.) and in gliadin (1·8 per cent.); D. B. Jones and C. O. Johns[8] have also isolated it from stizolobin, the globulin of the Chinese velvet bean (yield 2·8 per cent.). In dogs rendered diabetic by phloridzin, β-hydroxyglutamic acid appears as "extra glucose," as is the case with glutamic acid, proline and ornithine, and the amount was found to correspond closely with that derivable from three of the five carbon atoms. Dakin considers that β-hydroxyglutamic acid very likely arises in the body from glutamic acid and would then constitute an example of "β-oxidation" such as is known to occur in fatty acids, but has not yet been observed in amino-acids. Thus proline would be converted to glutamic acid via pyrrolidonecarboxylic acid, and ornithine would also be converted into glutamic acid. The latter would then be changed into dextrose by successive conversion into

[8] *J. Biol. Chem.*, 1919, **40**, 435 ; *A.*, i, 191.

β-hydroxyglutamic, malic and lactic acids, two molecules of the latter forming the hexose. In support of this view Dakin has oxidised β-hydroxyglutamic to malic acid *in vitro* and the biochemical conversion of the latter into sugars has been brought about in several ways.

A new method for preparing esters of amino-acids has been published by F. W. Foreman.[9] It consists in converting the amino-acids into their dry lead salts, which are suspended in absolute alcohol and esterified by saturating with hydrogen chloride. After removal of the free hydrochloric acid and the alcohol, the ester hydrochlorides are dissolved in dry chloroform and the free esters liberated by shaking with anhydrous barium hydroxide. Thus the considerable loss of esters by hydrolysis is avoided, which occurs in aqueous solution. The process has been applied to caseinogen and some of the deficit has been accounted for, without however taking Dakin's above-mentioned hydroxyglutamic acid into account. Although amino-acids are usually formulated with tervalent nitrogen and free carboxyl, they might also be represented as internal anhydrides of an acid with an ammonium hydroxide. This "betaine" formula, originally suggested by R. Willstätter, was supported experimentally by A. Geake and M. Nierenstein,[10] who found that amino-acids are not methylated in ethereal suspension by diazomethane. J. Herzig and K. Landsteiner[11] have confirmed this observation as regards glycine and alanine, but find that in other amino-acids the carboxyl group is slowly and at least partly esterified, so that in them there appears to be an equilibrium between the two forms thus:—

$$NH_2 \cdot CH_2 \cdot CO_2H \text{ and } \overline{NH_3 \cdot CH_2 \cdot CO \cdot O}.$$
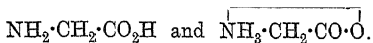
An unstable variety of glycine, differing from the ordinary one in crystalline form, has been described recently by H. King and A. D. Palmer.[12] Presumably this is the variety corresponding with the former of the above two formulæ, with a free carboxyl group, and it might be made to react with diazomethane. King and Palmer consider it probably identical with the fine needles which Emil Fischer obtained on precipitating an aqueous glycine solution with alcohol; it is the only variety of glycine that reacts with phosphorus pentachloride, which reaction also postulates a free carboxyl group. King and Palmer are mainly concerned with confirming the existence of compound of glycine with neutral salts,

[9] *Biochem. J.*, 1919, **13**, 378 ; *A.*, i, 338.
[10] *Zeitsch. physiol. Chem.*, 1914, **92**, 149 ; *A.*, 1914, i, 1057.
[11] *Biochem. Zeitsch.*, 1920, **105**, 111 ; *A*, i, 719.
[12] *Biochem. J.*, 1920, **14**, 576 ; *A*, i, 823.

described by Pfeiffer and his co-workers and called into question by Bayliss.

Hydroxyproline contains two asymmetric carbon atoms and in addition to the natural acid three stereoisomerides should exist. All have now been obtained by H. Leuchs and K. Bormann.[13] The puzzling transformation of tryptophan in the organism of the dog into kynurenic acid has now been almost certainly elucidated by A. Ellinger and Z. Matsuoka[14]; they synthesised indole-3-pyruvic acid and found that, like tryptophan, it is converted into kynurenic acid. The mechanism of the formation of this quinoline derivative would therefore presumably be as follows:—

$$\text{(indole)}\ C\cdot CH_2\cdot CH(NH_2)\cdot CO_2H \quad\longrightarrow\quad \text{(indole)}\ C\cdot CH_2\cdot CO\cdot CO_2H$$

$$\longrightarrow\quad \text{(ring)}-CO\cdot CH_2\cdot CO\cdot CO_2H \quad\longrightarrow\quad \text{(ring)}\ \begin{array}{c}CO\\ CH_2\\ CO\cdot CO_2H\end{array}\quad NH_2 \quad\longrightarrow$$

$$\text{(quinoline)}\ \begin{array}{c}C\cdot OH\\ CH\\ C\cdot CO_2H\end{array}\ N$$
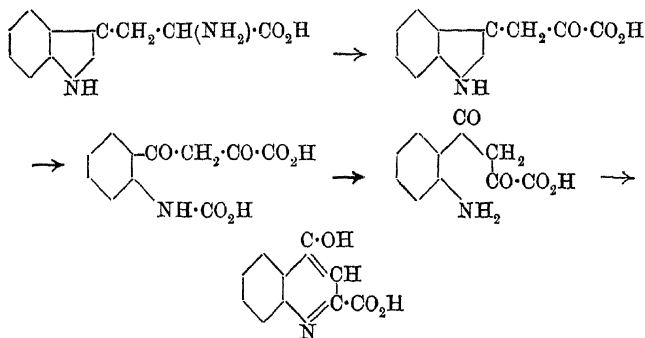
Here indolepyruvic acid figures as the first transformation product of tryptophan, which is in accordance with the known behaviour of other amino-acids.[15] As Ellinger and Matsuoka point out, the only criticism which can be urged is, that indolepyruvic acid is first transformed to tryptophan and that the amino-acid is converted into kynurenic acid by some other reaction, for it has been shown that, for instance, pyruvic acid itself may yield alanine, and phenylpyruvic acid phenylalanine, when perfused through the surviving liver. The hydroxyl group of kynurenic acid must be represented in its precursor, for quinoline-α-carboxylic acid is not oxidised to kynurenic acid in the dog, but is excreted partly unchanged, partly combined with glycine. The Hopkins-Cole test for tryptophan has been examined by W. R. Fearon[16] in a suggestive paper. Although the conclusions are based on

[13] *Ber.*, 1919, **52**, [B], 2086 ; *A.*, i, 185.

[14] *Zeitsch. physiol. Chem.*, 1920, **101**, 259 ; *A.*, i, 696.

[15] For example, F. Knoop and E. Kertess, *ibid.*, 1911, **71**, 252 ; *A.*, 1911, ii, 514.   [16] *Biochem. J.*, 1920, **14**, 548 ; *A.*, ii, 786.

molecular weight and nitrogen determinations only of amorphous pigments, and are therefore somewhat speculative, a considerable advance has been made, which ought to be useful in dealing with other substances (for example, alkaloids) related to tryptophan. Two molecules of indole, scatole, tryptophan or carbazole, were condensed with one molecule of an aldehyde (formaldehyde, glyoxylic acid, benzaldehyde) in *pure* glacial acetic acid by means of hydrogen chloride to leuco-compounds, which are oxidised to pigments, for example, for scatole.
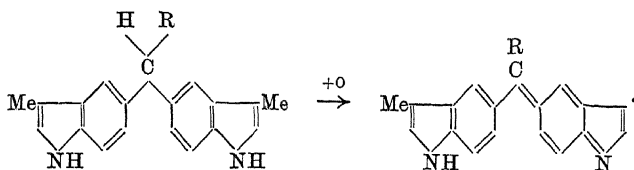
It will be seen that they are regarded as related to diphenyl-methane dyes. With tryptophan and formaldehyde or glyoxylic acid in the above-mentioned proportions the compounds are red, but with three molecules of the aldehyde to two of tryptophan blue compounds result, which are considered to arise from the condensa-tion of the two additional aldehyde molecules with the two trypto-phan side chains to form carboline derivatives of the type found in harman.[17] It is thus clear that blue compounds cannot be ob-tained from tryptophan combined as peptide, but red compounds might perhaps be expected in this case. As usually carried out, the Hopkins-Cole test results in a mixture of tryptophan red and blue.

Various colorimetric methods for estimating tryptophan have been examined by P. Thomas,[18] who prefers the use of *p*-dimethylaminobenzaldehyde as advocated by E. Herzfeld.[19] Thomas finds 1·7–1·8 per cent. in caseinogen, and as much as 2·3 per cent. in cerevisin, a protein from yeast, which is evidently able to form tryptophan from simpler compounds.

Similarly, L. Hugounenq and G. Florence[20] find that *Aspergillus* forms tryptophan when it has as only source of nitrogen any one of a series of natural amino-acids (it does not grow on phenyl-glycine). These authors also prefer *p*-dimethylaminobenzaldehyde for detecting tryptophan. The synthesis of tryptophan has also

[17] *Ann. Reports*, 1919, **16**, 156. W. H. Perkin and R. Robinson, *T.*, 1919, **115**, 967.
[18] *Bull. Soc. Chim. biol.*, 1914, **1**, 67 ; *A.*, i, 266.
[19] *Biochem. Zeitsch.*, 1913, **56**, 258 ; *A.*, 1913, ii, 1088.
[20] *Bull. Soc. Chim. biol.*, 1920, **2**, 13 ; *A.*, i, 466.

been investigated by W. J. Logie [21] in various bacteria, for example, *B. Coli*, which can form it from straight-chain compounds such as ammonium lactate and sodium aspartate, and also from free indole; the appearance of indole in some cultures may be attributed both to increased production and diminished consumption. The action of bacteria on amino-acids has been further studied in Japan by T. Sasaki [22] and his pupils. Thus K. Hirai [23] has found that *B. lactis aerogenes*, like yeast, forms tyrosol from *l*-tyrosine, but only in minute quantity. The same author [24] finds that a strain of *Proteus vulgaris*, capable of converting *l*-tyrosine into *d*-*p*-hydroxyphenyl-lactic acid, also converts histidine into *d*-β-iminazolyl-lactic acid. This new degradation of histidine should be compared with the production of urocanic (iminazolyl-acrylic) acid by bacilli of the *Coli* group, observed by H. Raistrick. [25] The curious difference in the stereo-chemical behaviour of *B. proteus* and *B. subtilis* originally observed by Sasaki for tyrosine, has been also demonstrated for *d*-*l*-phenylalanine by H. Amatsu and M. Tsudji. [26]

With Henderson's phosphate mixture phenyl-lactic acid and very little phenylethylamine is formed, *B. proteus* forming the dextro- and *B. subtilis* the laevo-variety of the acid. If instead of Henderson's mixture, uranyl phosphate and milk sugar are used as nutrient medium the amine is formed to the exclusion of the acid.

The Gases of the Blood.

This subject, more than any other, continues to occupy English physiologists, four out of the five papers in the current number of the *Journal of Physiology* are concerned with it. R. Wertheimer [27] has confirmed the observation hitherto only made accurately by R. A. Peters [28] that oxygen and hæmoglobin combine in molecular proportions as originally suggested by Hüfner. It should be noted, however, that Peters' values apply to hæmoglobin in the presence of dilute ammonia, and that Wertheimer only obtained agreement with these values in the presence of sodium carbonate; hæmoglobin dissolved in pure water had an oxygen

[21] *J. Path. Bact.*, 1920, **23**, 224; *A.*, i, 912.

[22] Compare *Ann. Reports*, 1917, **14**, 190, 191.

[23] *Acta Scholae Med. Univ. Kyoto*, 1918, **2**, 425; *A.*, i, 581.

[24] *Ibid.*, 1919, **3**, 49; *A.*, 1919, i, 612.

[25] *Ann. Reports*, 1917, **14**, 191; *A.*, 1917, i, 499; *Biochem. J.*, 1919, **13**, 446; *A.*, i, 348.

[26] *Acta Scholae Med. Univ. Kyoto*, 1918, **2**, 447; *A.*, i, 581.

[27] *Biochem. Zeitsch.*, 1920, **106**, 12; *A.*, i, 773.

[28] *J. Physiol.*, 1912, **44**, 131; *A.*, 1912, i, 519.

capacity 7 per cent. smaller. It is, however, the carbon dioxide in blood rather than the oxygen which stimulates work and controversy. We may first consider those authors who attempt to utilise the laws of mass action and of electrolytic dissociation to the full, without perhaps always considering sufficiently whether these laws apply to a colloidal solution like plasma or to a grossly heterogeneous system like whole blood.

T. R. Parsons[29] has attempted to calculate 'the carbon dioxide dissociation curve of blood on the assumption that a fixed amount of sodium is shared between two weak acids, namely, carbonic acid and hæmoglobin (with plasma proteins). The changes of reaction in blood due to increase of carbon dioxide pressure are much more gradual than in a sodium hydrogen carbonate solution because the proteins, and especially hæmoglobin, act as "buffers." Hæmoglobin would therefore have as important a function in carbon dioxide transport and maintenance of normal hydrogen ion concentration as in the transport of oxygen. The share of the plasma proteins (as distinct from hæmoglobin) in this buffer action is still a matter of dispute. If they act as buffers at all they must form ionised salts. A. R. Cushny[30] denies this; he filtered serum through collodion and found all the crystalloid constituents to be present in the same concentration in the filtrate as in the serum (with the exception of calcium and probably of magnesium). F. G. Hopkins,[31] on the other hand, evidently believes in the existence of ion-proteins. W. M. Bayliss[32] finds that the plasma proteins play no perceptible part in the maintenance of neutrality between limits of hydrogen ion concentration possible in the living organism. Parsons, in his second paper quoted above, considers that the weak acid competing with carbonic for the sodium is mainly, if not entirely, hæmoglobin. Using a similar conception, L. J. Henderson[33] has attempted to explain the simultaneous reaction of hæmoglobin with oxygen and with carbon dioxide. He is led to the assumption that a certain acid radicle of reduced hæmoglobin has a dissociation constant of $2 \cdot 3 \times 10^{-8}$, which is increased in oxyhæmoglobin to $2 \cdot 0 \times 10^{-7}$, thus expressing quantitatively an idea put forward by J. Christiansen, C. G. Douglas, and J. S. Haldane.[34] When the hæmoglobin thus becomes more electrolytically dissociated owing to its taking up oxygen, it also takes up

[29] J. Physiol., 1919, 53, 42, 340; A., i, 508.
[30] Ibid., 1920, 53, 391; A., i, 508.
[31] Brit. Med. J., 1920, ii, 70.
[32] J. Physiol., 1920, 53, 162; A., i, 507.
[33] J. Biol. Chem., 1920, 41, 401; A., i, 403.
[34] J. Physiol., 1914, 48, 244; A., 1914, i, 1012.

more base (sodium) and carbonic acid is set free. (This would be the process in the lungs; the reverse would occur in the tissues.) It is impossible to do more here than indicate the fundamental notion of Henderson's paper.

In such theoretical speculations it is important to remember the observation made 30 years ago by Hamburger that red blood corpuscles are permeable to chloride and phosphate ions; his pupil S. de Boer [35] more recently showed the same to be the case for sulphate ions. This ionic interchange between plasma and corpuscles has lately attracted the attention of a number of workers. L. S. Fridericia [36] finds that the increased chlorine content of the corpuscle can be demonstrated at low pressures of carbon dioxide in the plasma, for example, 0·1 atmosphere. The amount of chlorine gained by the corpuscles on increasing the carbon dioxide pressure from 0·08 to 162 mm. almost completely accounts for the increased carbon dioxide-combining power coincidently gained by the plasma. The hydrogen ion concentrations of plasma and corpuscles remain fairly constant. This is an extension of K. A. Hasselbalch's [37] attempt to explain that whereas a sodium hydrogen carbonate solution contains the same amount of carbon dioxide at all (except very low) pressures of the gas, in blood, on the other hand, the carbon dioxide-combining power increases with the pressure (as if bicarbonate had been added). Hasselbalch invokes the ampholyte character of hæmoglobin, which he conceives as having an acid character at low carbon dioxide pressures so that it displaces carbon dioxide from bicarbonate, and alkaline qualities at high carbon dioxide pressures, so that it combines with increasing amounts of carbon dioxide. The obvious question remained, how can hæmoglobin in the corpuscles influence bicarbonate in the plasma? Fridericia insists that the necessary link between the two phases is to be found in the wandering of the anions. H. Straub and K. Meier [38] have approached the same question by subjecting corpuscles in physiological saline to various concentrations of carbon dioxide. The corpuscles themselves act as buffers, their P_H being 7·00 when that of the solution was 6·67. The authors connect this effect with the partial permeability and the colloidal properties of the corpuscles. Their work has been discussed by L. Michaelis.[39] Working on somewhat similar lines, J. M. H. Campbell and E. P.

[35] *J. Physiol.*, 1917, **51**, 211; *A.*, 1917, i, 671.
[36] *J. Biol. Chem.*, 1920, **42**, 245; *A.*, i, 648.
[37] *Biochem. Zeitsch.*, 1916, **78**, 112; *A.*, 1917, i, 490.
[38] *Ibid.*, 1918, **89**, 156; **90**, 305; 1919, **98**, 205, 228. *A.*, 1918, ii, 467; 1919, i, 53; 1920, i, 200.   [39] *Ibid.*, 1920, **103**, 53; *A.*, i, 579.

Poulton [40] also find the isoelectric point of hæmoglobin at P_H 6·98 Under physiological conditions the blood proteins act as acids and do not themselves combine with carbon dioxide until the blood is much more acid than ever happens in the body. The partition of carbon dioxide between corpuscles and plasma at different carbon dioxide pressures has also been recently investigated by J. Joffe and E. P. Poulton [41] with results similar to those of Straub and Meier. The former authors criticise D. D. van Slyke and G. E. Cullen's method, [42] for the determination of the alkali reserve, because the venous plasma, *after the separation of the corpuscles*, is brought into equilibrium with alveolar carbon dioxide, so that an ionic interchange with the corpuscles can no longer take place.

In most of the above papers carbon dioxide is not considered to be combined with the blood proteins, but to be entirely present as bicarbonate (at least under physiological conditions). This view is opposed by G. A. Buckmaster, [43] who revived Bohr's conception of a direct combination between carbon dioxide and hæmoglobin. A third view has recently been put forward by J. Mellanby and C. J. Thomas [44] in a paper which contains some novel experiments and views running counter to the current conception. These authors studied more particularly the ash associated with the blood proteins under various conditions. For instance, the protein precipitated from serum by adding an equal volume of alcohol at −10° is associated with a large amount of inorganic salt. When redissolved in water this protein combines with more carbon dioxide than can be calculated as existing in combination with the alkaline salt; from this and other experiments Mellanby and Thomas conclude that the carbon dioxide is adsorbed, chiefly on the fibrinogen, and that the proteins effect the transport of carbon dioxide. Since a 0·2 per cent. solution of sodium hydrogen carbonate is not precipitated by an equal volume of alcohol at −10°, it is incidentally concluded that this salt does not exist free in serum. The authors consider the bicarbonate hypothesis inadmissible (according to which the sodium is shared between carbonic and another weak acid). Sodium hydrogen carbonate with protein constitutes the alkali reserve. In shed blood lactic acid is produced from the corpuscles and that is why the carbon dioxide of shed blood falls steadily, and why this gas can be extracted completely from blood in a vacuum, but not from serum.

It seems to the writer that if the bicarbonate is adsorbed by the

[40] *J. Physiol.*, 1920, **54**, 152.
[41] *Ibid.*, 129.
[42] *Ann. Reports*, 1917, **14**, 173.
[43] *Ibid.*, 1918, **15**, 147.
[44] *J. Physiol.*, 1920, **54**, 178.

serum proteins, the latter still may transport carbon dioxide as salt, in accordance with the view more generally accepted. Mellanby and Thomas lay great stress on the colloidal properties of serum and support the doubt, expressed above, that the laws of equilibrium in homogeneous systems are not immediately applicable to this case.

The estimation of carbon monoxide in blood and of the latter's CO-capacity has been described by M. Nicloux.[45]

An interesting contribution to the technique of determining the hydrogen-ion concentration of blood has been made by H. H. Dale and C. L. Evans.[46] They dialyse about 5 c.c. of oxalated blood into 1 c.c. of saline, avoiding loss of carbon dioxide. The P_H of the dialysate is then found colorimetrically, by mixing phosphate solutions until the mixture gives with neutral-red the same colour as the dialysate. The method appears to be very convenient and accurate, and may well be applicable to fluids other than blood. The regulation of the blood's alkalinity has been investigated by H. W. Davies, J. B. S. Haldane, and E. L. Kennaway,[47] who find at high carbon dioxide-pressures a considerable deviation from Parsons' theoretical dissociation curve, referred to above. They studied the effect of eating large quantities of sodium hydrogen carbonate, which produces increased carbon dioxide-capacity of the blood, increase in alveolar carbon dioxide, rapid excretion of bicarbonate in the urine, disappearance or great decrease of urinary ammonia and sometimes appearance of acetone substances. These effects illustrate the way in which the organism compensates for alkalosis by changed respiration and metabolism. The ammonia normally excreted in the urine would ultimately appear as neutral urea and the acid normally combined with it becomes available for neutralising the alkali ingested. For the related subject of acidosis reference can here only be made to papers by H. W. Haggard and Y. Henderson.[48]

Accessory Food Substances.

The name vitamines is all but established, in spite of the fact that it suggests a relationship to amines, of which there is no proof. J. C. Drummond[49] suggests a compromise by dropping the final " e," so as not to suggest basic properties (to those familiar with the Chemical Society's nomenclature). He further calls fat-soluble-*A*

[45] *Bull. Soc. Chim. biol.*, 1920, **2**, 171.
[46] *J. Physiol.*, 1920, **54**, 167.   [47] *Ibid.*, 32.
[48] *J. Biol. Chem.*, 1920, **43**, 3, 15.
[49] *Biochem. J.*, 1920, **14**, 660 ; *A.*, i, 908.

and water-soluble-*B*, simply vitamin-*A*, vitamin-*B*, etc.   Work
on accessory food substances is going on with unabated vigour in
England and in America; there are also signs of increased interest
in and recognition of the subject in France and in Germany.   On
account of its great value, we may once more refer here to the
Special Report No. 38 of the Medical Research Committee (now
Research Council), which survey was mentioned in last year's
Report.

It seems that the resistance of some accessory food factors to
high temperatures has been somewhat underestimated.   Thus H.
Steenbock and P. W. Boutwell[50] now report that the fat-soluble
vitamin-*A* of yellow maize is unaffected by heating for three hours
under 7 kilos pressure, nor does this treatment appreciably diminish
the same factor in chard, carrots, sweet potatoes and squash.   The
relative stability of vitamin-*A* is also insisted on by T. B. Osborne,
L. B. Mendel and A. J. Wakeman,[51] who cannot confirm the
great thermolability formerly attributed to this substance from
animal sources by H. Steenbock, P. W. Boutwell and H. E. Kent,[52]
and by J. C. Drummond.[53]   The explanation of this discrepancy
is probably found in an experiment described by F. G. Hopkins[54]
in opening a discussion on vitamins in clinical medicine at the
annual meeting of the British Medical Association last July.   But-
ter fat heated for four hours to 120° without aeration remains
active, but when a stream of air is bubbled through it during the
heating, it becomes inactive.   It seems that the fat-soluble vitamin
possesses considerable heat-stability but is easily oxidised.   That
vitamins are readily destroyed by oxidation seems also to result
from the fact, related by A. F. Hess,[55] that milk or neutralised
canned tomato juice loses much of its activity by being shaken
with air for half an hour.   The deleterious effect sometimes ob-
served in pasteurised milk may be the result of exposure to warm
air rather than a simple temperature effect.   G. F. Still[56] points
out that so-called "buddized milk," sterilised by being warmed
with hydrogen peroxide to 50°, was found clinically to have lost its
anti-scorbutic properties.   Laboratory experiments on the effect of
suitable oxidising agents on the various vitamins at room
temperature now seem desirable.   Similarly, E. M. Delf[57] finds
that the anti-scorbutic vitamin-*C* of orange and swede juice has

[50] *J. Biol. Chem.*, 1920, **41**, 163 ; *A.*, i, 358.
[51] *Ibid.*, 549 ; *A.*, i, 457.
[52] *J. Biochem.*, 1918, **35**, 517 ; *A.*, 1918, i, 513.
[53] *Biochem. J.*, 1919, **13**, 81 ; *A.*, 1919, i, 363.
[54] *Brit. Med. J.*, 1920, ii, 147.
[55] *Ibid.*, ii, 154.   [56] *Ibid.*, ii, 156.
[57] *Biochem. J.*, 1920, **14**, 211 ; *A.*, i, 460.

an unexpectedly great stability above 100° if the heating is conducted in the absence of air. The practical bearing of these experiments on canning and other methods of food-preservation is obvious and the same applies to those of A. Harden and R. Robison,[58] who find that with suitable precautions orange juice may be evaporated to dryness without loss of activity and that the dry residue retains much of its activity after two years' storage.

A few further attempts have been made to isolate the water-soluble antineuritic vitamin-*B*, which for various reasons seems to hold out more hope than vitamins-*A* or -*C*. The most interesting of these attempts is that made by F. Hofmeister and M. Tanaka,[59] who during the war isolated from rice polishings a base *oridine*, $C_5H_{11}O_2N$, which as crude hydrochloride cured polyneuritis of pigeons in small doses, but became inert when purified for analysis. Either the antineuritic vitamin was a mere impurity in the crude crystals and therefore extraordinarily active, or the active substance underwent chemical transformation during the process of purification (regeneration from aurichloride and recrystallisation of the hydrochloride so obtained). Although the empirical formula of oridine is the same as that of valine, the substance appears to be more closely related to pyridine and is possibly a dihydroxypiperidine. The result reminds one of C. Funk's earlier investigations when the antineuritic substance was associated with nicotinic acid. C. N. Myers and C. Voegtlin,[60] using methods for the isolation of bases somewhat similar to those employed by Funk, obtained from dried yeast a crystalline antineuritic substance which became inactive on drying. The method of extracting vitamin-*B* from rice bran has been studied by B. C. P. Jansen,[61] who states that an alcoholic extract of rice polishings is now used in Java against beri-beri. He used 0·3 per cent. aqueous hydrochloric acid, or 70 per cent. alcohol, or 96 per cent. alcohol with $\frac{1}{15}$ volume of concentrated hydrochloric acid, and found that with each solvent the vitamin is completely extracted in two days. He criticises curative experiments with pigeons as being uncertain unless much time is expended on them; it is better, and not necessarily slower, to find the minimum preventive dose which must be added to a diet of polished rice. Much time may be saved by using a small species of Indian bird (*Musica maja*), which is far more sensitive than the pigeon.

The results obtained in the laboratory with animals are now

[58] *Biochem. J.*, 1920, **14**, 171 ; *A.*, i, 460.

[59] *Biochem. Zeitsch.*, 1920, **103**, 218 ; *A.*, i, 586.

[60] *J. Biol. Chem.*, 1920, **42**, 199 ; *A.*, i, 500.

[61] *Mededeelingen Geneesk. Lab. Weltevreden*, 1920, [iii], A, 23.

more and more being put to clinical use, most of all in Vienna.[62] Charts [63] giving the effect of butter or cod liver oil and fresh turnip juice, added to the diet of nursing mothers or of infants, demonstrate the same remarkable effect on the body weight of the children as has been studied in animals. Turnip juice contains the antiscorbutic vitamin and is a cheap substitute for lemon juice; its clinical value has now also been emphasised in Germany.[64] Various gastro-intestinal disorders in adults are now attributed by R. McCarrison [65] to vitamin deficiency and he has found, for instance, that healthy monkeys, carriers of *Entamœba* cysts, develop dysentery when placed on devitaminised food.

Evidence is accumulating that vitamins are not only necessary for animals, but also for some fungi. R. J. Williams,[66] F. M. Bachmann,[67] W. H. Eddy, and H. C. Stevenson [68] estimate the strength of vitamin (*B* ?) solutions by growing yeast cells in them. In his second paper Williams has made the method gravimetric by weighing the yeast. The method has been adversely criticised by G. de P. Souza and E. V. McCollum,[69] who find that many substances stimulate the growth of yeast. Pasteur already failed to grow yeast from a single cell in synthetic media, and Wildier [70] postulated a special substance, "bios," necessary for the growth of yeast cells. A similar relationship seems to hold for *Sclerotinia cinerea*, the fungus causing brown rot in peaches and plums; according to J. J. Willaman,[71] it does not grow on synthetic media sufficing for *Aspergillus*, for example, but it will grow when a "vitamin" preparation is added, obtained by means of adsorption by fullers' earth from a variety of animal and vegetable sources. This substance, like "bios," is thought to be identical with water-soluble vitamin-*B*, but such a speculation is of course incapable of exact verification as long as vitamins have not been isolated. Indeed, the identity of the growth-promoting water-soluble vitamin with the antineuritic, now generally presumed, is denied by A. D. Emmett in conjunction with G. O. Luros [72] and with M. Stockholm.[73] That vitamins are necessary for fungi is also denied; A. Lumière [73a] finds that yeast heated to 135° and no longer capable

[62] (Miss) H. Chick, *Brit. Med. J.*, 1920, ii, 131. [63] E. J. Dalyell, *ibid.*, ii, 132.

[64] H. Aron and S. Samelson, *Deutsch. med. Woch.*, 1920, **46**, 772.

[65] *Brit. Med. J.*, 1920, i, 822.

[66] *J. Biol. Chem.*, 1919, **38**, 465; 1920, **42**, 59; *A.*, 1919, i, 463.

[67] *Ibid.*, 1919, **39**, 235; *A.*, 1919, i, 613.

[68] *Ibid.*, 1920, **43**, 295; *A.*, ii, 716.

[69] *Ibid.*, 1920, **44**, 113; *A.*, i, 919. [70] *La cellule*, 1901, **18**, 313.

[71] *J. Amer. Chem. Soc.*, 1920, **42**, 549; *A.*, i, 412.

[72] *J. Biol. Chem.*, 1920, **43**, 265; *A.*, i, 698.

[73] *Ibid.*, 287; *A.*, i, 701. [73a] *Compt. rend.*, 1920, **171**, 271; *A.*, i, 653.

of curing polyneuritis gives a bouillon which greatly improves the development of fungi. From what has been said above it will be seen that Lumière's experiments are not necessarily in conflict with those of Williams and of Bachmann. Heating to 135° may not have left enough vitamin to cure pigeons; yet there might be enough to have a favourable effect on the growth of yeast. It is even more difficult to judge of the vitamin-nature of the crude nucleic acid derivatives in bacterised peat, which according to W. B. Bottomley [74] favour the growth of *Lemna* in water culture. Experiments on the growth-promoting substances in various organic manurial composts by F. A. Mockeridge [75] seem to depend more definitely on the presence of purine and pyrimidine bases in these manures.

Pellagra, a disease occurring in countries (Italy, Carolina) where maize is the principal article of diet, has of late years been more and more considered due to a dietary deficiency, and it has been suggested that the cause lies in the absence of tryptophan and perhaps also of lysine from zein, the chief protein of maize. The metabolic importance of the former amino-acid was established by E. G. Willcock and F. G. Hopkins [76] in the case of young mice, that of the latter by T. B. Osborne and L. B. Mendel.[77]

Occasional outbreaks of pellagra in institutions, camps, etc., have always cleared up on the inclusion of more milk, meat, eggs or cheese in the dietary, but whether the cure was due to tryptophan in caseinogen is not thoroughly established. H. Chick and E. M. Hume [78] describe experiments with monkeys on a diet rich in all known vitamins, but with zein as its principal protein. Symptoms closely resembling those of pellagra were produced and were undoubtedly of dietary origin. In one case they cleared up rapidly when caseinogen was administered as well, but the crucial point, whether it was tryptophan which made the difference, could not be established with certainty. This amino-acid appeared to have a beneficial effect, but no cure was effected with it alone.

Ferments.

The discussion on the diastase-like properties of formaldehyde, which has been carried on in Germany during the last few years, may be mentioned here, not so much as a contribution to our know-

[74] *Proc. Roy. Soc.*, 1920, [B], **91**, 83 ; *A.*, i, 265.
[75] *Biochem. J.*, 1920, **14**, 432 ; *A.*, i, 704.
[76] *J. Physiol.*, 1906, **35**, 88 ; *A.*, 1907, ii, 88.
[77] *J. Biol. Chem.*, 1914, **17**, 325 ; *A.*, 1914, i, 620.
[78] *Biochem. J.*, 1920, **14**, 135.

ledge of enzymes, but rather as a curious example of scientific controversy. G. Woker and H. Maggi have repeatedly asserted, both separately and together,[79] that formaldehyde has the power of hydrolysing starch. They have been attacked by various critics in a number of separate papers, and finally these critics have banded themselves together in a final onslaught.[80] The explana- tion of the supposed diastatic action of formaldehyde lies in the fact that the latter forms a loose additive compound with starch (which compound does not give a blue colour with iodine), and that formaldehyde also modifies the physical properties of the colloid. This view is shared by E. Herzfeld and R. Klinger,[81] who hold similar views as to the action of formaldehyde and for- mulate, in addition, somewhat revolutionary ideas on starch hydro- lysis, according to which the formation of dextrins (including achroodextrins) may be a purely physical change in the degree of dispersion, without any hydrolysis. The hydrolysis of starch (by amylase) is also discussed in a suggestive, largely theoretical paper by L. Ambard, E. Pelbois and M. Bricka,[82] who consider it to be just as much a unimolecular reaction as the hydrolysis of sucrose by acids. The action of neutral salts is similar, accelerat- ing the latter, and making possible the former action (dialysed saliva is without action on starch). In either case the action of the neutral salt is on the *substrate,* not on the catalyst. For starch the action depends on the anion and is greatest for chlorides, at P_H 6·45, which gives also the reaction of a solution in which the amylase is most stable. Under these conditions the optimum con- centration of sodium chloride is 0·006 molar, but in this neigh- bourhood considerable changes in the salt concentration do not very much affect the rate of hydrolysis.

Potato tyrosinase has been separated by H. Haehn[83] into two components by means of a Bechhold ultra-filter. The residue is thermolabile " α-tyrosinase," the filtrate is an " activator " which retains its activity after incineration. In the case of a successful separation (which is not always possible), the two components are separately inactive on tyrosine, but become so when mixed.

It is natural that attempts have been made to demonstrate the reversibility of hydrolytic action in such a simple and specific case as that of urease, and H. P. Barendrecht,[84] in developing a radia-

[79] For example, *Ber.,* 1919, **52,** [B], 1594 ; *A.,* i, 10.

[80] M. Jacoby, W. von Kaufmann, A. Lewite, and H. Sallinger, *ibid.,* 1920, **53,** [B], 681 ; *A.,* i, 424.   [81] *Biochem. Zeitsch.,* 1920, **107,** 268 ; *A.,* i, 713.

[82] *Bull. Soc. Chim. biol.,* 1920, **2,** 42.

[83] *Ber.,* 1919, **52,** [B], 2029 ; *A.,* i, 102 ; *Biochem. Zeitsch.,* 1920, **105,** 169 ; *A.,* i, 777.

[84] *Proc. K. Akad. Wetensch. Amsterdam,* 1919, **22,** 29, 126 ; *A.,* i, 102, 195.

tion theory of enzyme actions, claims that urease under certain conditions can transform ammonium carbonate into urea. This is denied by T. J. F. Mattaar.[85] In any case urease undergoes more or less rapid destruction in a solution of ammonium carbonate.

E. Yamasaki[86] has investigated the kinetics of urease and considers that the hydrolysis of urea is a simple catalytic action carried on in the substrate phase and does not consist in the decomposition with measurable velocity of an intermediate compound formed instantaneously. Nor do the enzyme and substrate form an intermediate compound with measurable velocity. The addition of electrolytes diminishes the activity of the enzyme owing to adsorption by the latter, and the effect may in various cases be expressed according to Freundlich's adsorption formula. Perhaps it is the electrolyte nature of ammonium carbonate which prevents the reversibility of the urease action from being demonstrated.

The same author[87] has compared the temperature-coefficients for the destruction of catalase from bamboo shoots, germinated soja beans and blood. As the coefficient is different in each case, he concludes that the enzymes are also different. The effect of " poisons " is considered to be due to adsorption by and coagulation of the enzyme. C. G. Santesson[88] also considers that the effect of electrolytes on the rate of the catalase action is due to adsorption and finds that the anions can be arranged in Hofmeister's lyotropic series, SO_4 having the smallest and CN the greatest inhibitory effect. C. Neuberg and F. F. Nord[89] have extended the reduction, by yeast, of the carbonyl group from aldehydes to ketones. In the latter case they get *optically active* secondary alcohols in yields of about 10 per cent. Diacetyl yields *l*-βγ-butylene glycol, whereas Harden and Walpole found that bacteria produce from carbohydrates a mixture of the racemic and meso-forms. Another interesting product of ferment action is the crystalline specimen of sucrose obtained by E. Bourquelot and M. Bridel,[90] by the action of emulsin on gentianose. Previously this trisaccharide had only been hydrolysed to fructose and gentiobiose by invertase, and then the latter sugar could be split into two molecules of dextrose by "gentiobiase" of bitter almonds. The authors were, however, led to attempt a different degradation by the simultaneous occurrence of sucrose and gentiobiose in fresh

[85] Rec. trav. chim., 1920, **39**, 495 ; A., i, 649.

[86] Sci. Rep. Tôhoku Imp. Univ., 1920, **9**, 97 ; A., i, 577.

[87] Ibid., 1920, **9**, 13, 59, 75, 89 ; A., i, 194, 453, 574, 576.

[88] Skand. Arch. Physiol., 1920, **39**, 236 ; A., i, 576.

[89] Ber., 1919, **52**, [B], 2237, 2248 ; A., i, 135.

[90] Bull. Soc. Chim. biol., 1920, **2**, 160 ; Compt. rend., 1920, **171**, 11 ; A., i, 530.

gentian root. They finally succeeded by using a specimen of bitter almonds as free as possible from invertase, and controlling the length of the reaction polarimetrically.

Estimation and Formation of Urea.

Hypobromite does not liberate the whole of the nitrogen from urea and the addition of substances like dextrose has been shown by M. Krogh[91] to give illusory results, since carbon monoxide is given off. L. Ambard[92] now criticises Krogh's high results because oxygen is also evolved. After absorption of this gas by sodium hyposulphite the nitrogen corresponds with 90 per cent. of the theoretical. Apart from the use of urease, a more elegant method of estimating urea is that given by R. Fosse,[93] which does not appear to have received in this country the attention it deserves. It is based on the fact that xanthhydrol precipitates urea at dilutions as high as 1 : 1,000,000. The method has been recently critically examined and favourably reported on by Frenkel.[94] With its aid Fosse has lately studied the formation of urea by oxidising proteins with permanganate, first observed by Béchamp in 1856, but afterwards denied. Ordinarily only small amounts are produced, but if the oxidised solution is subsequently heated with ammonium chloride, much larger quantities of urea result,[95] because the solution contains cyanic acid.[96] When dextrose is added during oxidation the yield of urea is also much increased and small quantities of dextrose alone, in the presence of concentrated ammonium hydroxide, may yield 70 per cent. of the sugar as urea.[97] The reaction is considered to proceed through the stages: formaldehyde, hydrocyanic acid, cyanic acid, ammonium cyanate, and it is suggested that this explains the formation of urea in plants. Under certain conditions a little oxamide may also be formed.[98]

[91] *Zeitsch. physiol. Chem.*, 1913, **84**, 379 ; *A.*, 1913, ii, 641.

[92] *Bull. Soc. Chim. biol.*, 1920, **2**, 205 ; *A.*, 1921.

[93] *Compt. rend.*, 1914, **158**, 1076, 1588 ; **159**, 250 ; *A.*, 1914, ii, 506, 593, 756 ; *Ann. Reports*, 1914, **11**, 178.

[94] *Ann. Chim. anal.*, 1920, [ii], **2**, 234 ; *A.*, ii, 646. Compare also P. Carnot, P. Gérard and S. Moissonnier, *Compt. rend Soc. Biol.*, 1919, **82**, 1136 ; M. Laudat, *ibid.*, 1920, **83**, 730 ; *A.*, ii, 645 ; W. Mestrezat and M. Janet, *ibid.*, 1920, **83**, 763 ; *A.*, ii, 645, 779.

[95] *Compt. rend.*, 1919, **168**, 320 ; *A.*, 1919, i, 152.

[96] *Ibid.*, 1919, **169**, 91 ; *A.*, 1919, i, 459.

[97] *Ibid.*, 1919, **168**. 1164 ; *A.*, 1919, i, 313.

[98] *Compt. rend.*, 1920, **171**, 398 ; *A.*, i, 664.

Hormones.

During the current year several attempts have been made to isolate the physiologically active principles of the pituitary body, but the position seems to be rather less hopeful than last year when J. J. Abel and S. Kubota [99] suggested that the plain muscle stimulant of pituitary might be identical with histamine. This suggestion was promptly rejected by D. Cow [1] and at once reaffirmed by J. J. Abel and D. I. Macht.[2] The attack and defence were made on purely pharmacological grounds, and may be cited as an illustration of the difficulties involved in settling the identity or non-identity of substances exclusively by their physiological action, without the chemical isolation of both. The differences in the physiological behaviour of the two substances, used by Cow in sup-port of his argument, were considered by Abel and Macht to be the result of differences in dosage. The notion that the pituitary uterine stimulant (oxytocic principle) is merely histamine was also rejected on more chemical evidence by H. W. Dudley,[3] who extracted the dry powdered gland with acidulated water and purified the extract with colloidal ferric hydroxide, which leaves the active principle entirely in solution. It can then be removed completely without loss by continuous extraction with butyl alcohol (under reduced pressure, so as to lower the temperature). The substance from pituitary is not identical with histamine, because, unlike this amine, it is destroyed at room temperature by N-sodium hydroxide, and further, because it is destroyed by trypsin, is extracted from *acid* solution by butyl alcohol, and is insoluble in boiling chloroform. As the result of Dudley's experiments and later ones of their own, J. J. Abel and T. Nagayama [4] have had to abandon the hope that the pituitary uterine stimulant is histamine. They nevertheless claim that infundibular extracts from fresh glands contain a little histamine, but much less than extracts of commercial dried gland previously examined by them, or than the extracts commonly employed in therapeutics. They suggest that the specific active principle, on boiling and sterilisa-tion, partly breaks down to histamine. The fact that they ob-tained an impure substance which is many times more oxytocic than histamine itself, is in itself sufficient to dispose of their previous suggestion that the two are identical. It also makes the chances of isolation much smaller—evidently this pituitary prin-

[99] *Ann. Reports*, 1919, **16**, 158. [1] *J. Pharm. Expt. Ther.*, 1919, **14**, 275.
[2] *Ibid.*, 279. [3] *Ibid.*, 295; *A.*, i, 344.
[4] *Ibid.*, 1920, **15**, 347.

ciple is a substance of quite extraordinary potency and present in very small amount.

M. T. Hanke and K. K. Koessler[5] go further than Abel and Nagayama, and deny that histamine is present at all in fresh pituitary; they partly rely on a colorimetric method for estimating histamine,[5a] and they incidentally cite a number of chemical and physiological differences between the amine and the pituitary principle. With regard to the latter, F. Fenger and M. Hull[6] state that in the fresh gland it is united to a protein complex and is insoluble in 95 per cent. alcohol, which, however, on boiling splits off a highly active, hygroscopic substance, more readily decomposed than its precursor. Of late most writers, for instance, Dudley[3] and C. Crawford,[7] consider the uterine and the pressor principle of pituitary to be distinct. According to the latter, the pressor principle gives no Millon reaction and only a very doubtful Pauly reaction, but on keeping an aqueous solution it becomes reactive to Pauly's reagent. Abel and Macht find that the Pauly reaction is always given by active preparations. In spite of the great therapeutical importance of the pituitary, the prospects of isolating any specific active principle from it do not appear to be very bright.

L. Stern and E. Rothlin[8] have prepared an impure substance from the spleen which they call "liénine"; it acts on smooth muscle very much like histamine, and has some of the chemical properties of the latter substance. The chief difference appears to be that liénine is destroyed by 1 per cent. sodium hydroxide, and histamine is not. Of a number of organ extracts examined as regards their action on smooth muscle fibre, that of the spleen is by far the most potent and the active substance is stated to be present in the blood of the splenic vein. Further chemical work is required to prove or disprove its identity with histamine.

Thyroxine was referred to at some length in last year's Report. Since then a long paper by E. C. Kendall and A. E. Osterberg[9] has come to hand, containing numerous microphotographs of crystals. Many analyses of thyroxine and its derivatives are now given for the first time, and the conditions governing the transformation of the ketonic or lactam into the enolic or lactim form and into the open chain hydrate are discussed. It is stated that the position of the three iodine atoms is determined by

[5] J. Biol. Chem., 1920, 43, 557.   [5a] Ibid., 543; A., 784.

[6] Ibid., 1920, 42, 153.

[7] J. Pharm. Expt. Ther., 1920, 15, 81; A., i, 458.

[8] J. Physiol. Path. gén., 1920, 18, 753: A., i, 649.

[9] J. Biol. Chem., 1919, 40, 265; A, i, 180.

synthesis, a description of which is promised later. Meanwhile E. C. Kendall has further developed the estimation of iodine in the thyroid; he thinks it best to use only 0·5 gram of the gland. E. C. Kendall and F. S. Richardson [10] find that there is 0·013 mg. of iodine in 100 c.c. of normal blood.

GEORGE BARGER.

[10] *J. Biol. Chem.*, 1920, **43**, 161 ; *A.*, ii, 631.   Compare also S. B. Kuzirian, *Proc. Iowa Acad. Sci.*, 1918, **25**, 495 ; *A.*, ii, 445.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

Much steady progress has to be reported, although no development of outstanding importance has occurred.

The outlook for the future is in some directions rather uncertain. The Woburn Fruit Farm, long carried on at the expense of the Duke of Bedford, and made famous by the important investigations of the late Spencer U. Pickering, will be closed before this Report appears; and at the moment of writing there is the possibility that the Woburn Experimental Station of the Royal Agricultural Society may be closed in 1921, although some hope still remains that this misfortune may be mitigated, or even averted. It seems probable that the research in agricultural science done by Germany and Austria will be less in future than it was before the War. As against that, however, the Ministry of Agriculture in this country has produced an admirable scheme, whereby the research institutes can attract the ablest of the younger men and women from the universities, and it may safely be said that the institutes were never before as well staffed as they are now. Both in amount and quality, the work in hand at the various centres of agricultural research in this oountry is full of promise for the future. Fortunately, also, in spite of the centralisation which is being forced by inexorable circumstances, there still remain independent outside critics who can save the workers at the institutes from the dangers of futility.

Soil.

It seems possible that the nature of the black organic matter in the soil, commonly known as "humus," will soon be understood.

Humus is formed from cellulose in the soil; no great amount seems to be obtained from the protein in plant residues. Maillard showed some years ago that a substance resembling humus is produced when sugar is heated either with mineral or amino-acids; in the latter case, the "humus" contains nitrogen, as in soil.

The reaction has been further investigated by V. A. Beckley in the Rothamsted laboratories; [1] setting out from an observation by Fenton, he showed that sugars, on treatment with acids, give rise to hydroxymethylfurfuraldehyde, which readily condenses to form a substance closely resembling humus. He also found indications of the presence of hydroxymethylfurfuraldehyde in a dunged soil and in rotting straw in which humus was being produced. He suggests, therefore, that the formation of humus in soil proceeds in two stages:

Carbohydrate (cellulose, etc.) + amino-acid =
$$\text{hydroxymethylfurfuraldehyde.}$$
Hydroxymethylfurfuraldehyde + amino-acid =
$$\text{humus} + \text{furfuraldehyde} + CO_2 \text{ by condensation.}$$
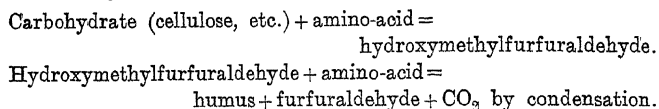
An alternative view is put forward that humus is derived from the oxidation of quinones.[2]

The humus has acid properties, which, however, are very difficult to measure. An interesting series of papers has been published [3] by S. Odén, of Upsala, one of the most ingenious of present-day workers on this difficult subject. He shows that selective absorption, once invoked to account for the acidity, can really play but a very minor part, since treatment of washed peat with potassium chloride solution gives no hydrochloric acid, but only non-volatile acids. Nor did iron or aluminium occur in the solution. Humic acid is a true acid; [4] it appeared, however, from the high P_H value of peat extracts that other organic acids were present as well. A method is described for obtaining neutralisation curves which will probably prove distinctly helpful to investigators.

He further discusses the effect of lime on peat.[5] It is well known that large quantities of lime—one or two tons per acre— are necessary in order to allow of the growth of agricultural crops on peat soils; whilst on normal soils much smaller quantities suffice. The usual explanation is that peat contains some harmful substance put out of action by lime. Odén shows that humic acid is so insoluble that it can hardly do much harm to vegetation; he also controverts Baumann and Gully's view that injury arises by absorptive decomposition of nutritive salts with liberation of acid. Further, he demonstrates by the old van Bemmelen method that lime effects no improvement in the fundamental water relation-

[1] *J. Agric. Sci.*, 1920, **11**, 69.

[2] W. Eller and K. Koch, *Ber.*, 1920, **53**, [B], 1469; *A.*, i, 733.

[3] *Int. Mitt. Bodenk.*, 1920, **9**, 361; he has also published a monograph dealing with the whole question of humus: *Koll. Chem. Beihefte*, 1919, **10**, 75.

[4] For further confirmation, see F. Fuchs, *Chem. Zeit.*, 1920, **44**, 551; *A.*, i, 596.   [5] *Int. Mitt. Bodenk.*, 1920, **9**, 375.

ships of peat. He concludes that humic acid is not itself harmful to plants, but, on the other hand, the calcium humate formed when lime is added to peat is distinctly beneficial, probably by acting as a "buffer" in regulating the hydrogen-ion concentration of the soil. It would react with harmful acids, forming harmless calcium salts and insoluble, harmless humic acid, thus maintaining the soil reaction suitable for plants and micro-organisms.

He also describes a colorimetric method for estimating the amount of humic acid in soil.[6] The problem is complicated by the fact that two intensely dark-coloured substances occur, namely, humic acid and the so-called hymatomelanic acid, in addition to the faintly coloured acids formerly known as crenic and apocrenic acids, but named "fulvic" by Odén.[7]

As separation of the two dark-coloured acids is not easy, a detailed examination was made of the absorption spectra of their sodium salts as well as of that of Merck's "acidum huminicum"; from the curves and data thus obtained the details of the method are worked out.

An aqueous extract of peat undergoes considerable changes on keeping, which have been examined in some detail.[8]

The organic phosphorus compounds of the soil have been studied in Ohio.[9] About one-third of the total phosphorus in the surface soil and one-fifth of that in the subsoil is found to be in this form, and this organic phosphorus is related both to the "humus soluble in ammonia," of which it forms about 1 per cent., and to the total nitrogen, being one-tenth the amount of the latter. There was no evidence that the organic phosphorus compounds have much direct nutrient value to plants, although they apparently undergo decomposition, since the amount in virgin soil is considerably above that in cultivated soil containing approximately the same quantity of total phosphorus.

The black organic matter insoluble in alkalis is known as "humin"; a similar-looking insoluble product is obtained by the interaction of amino-acids and tryptophan, tyrosine and formaldehyde.[10]

Soil Acidity.—Much work continues to be done in America on

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[6] *Int. Mitt. Bodenk.*, 1920, **9**, 391.

[7] The multiplication of definite names for indefinite soil acids is confusing : it would be better to adopt the biological plan, and speak of 'A,' 'B,' 'C,' etc., terms which can easily be discarded when more precise definition is possible.

[8] H. Puchner, *Kolloid Zeitsch.*, 1919, **25**, 196 ; 1920, **26**, 159 ; *A.*, i, 274, 468.

[9] C. J. Schollenberger, *Soil Sci.*, 1920, **10**, 127.

[10] R. A. Gortner and G. E. Holm, *J. Amer. Chem. Soc.*, 1920, **42**, 632, 821 ; *A.*, i, 400, 450.

soil acidity. Four explanations have been offered of the power
of soil to turn blue litmus red: selective adsorption (Cameron),
the presence of organic acids (Sprengel), of acid silicates (Hopkins,
Loew), of easily hydrolysable iron or aluminium salts which arise
when supplies of basic calcium and magnesium compounds are
low[11] (Abbott, Conner and Smaller, Daikuhara).

The existence of a definite hydrogen-ion concentration in acid
soils shows the presence of definite acids, without, however, giving
much information as to their nature.[12]

Aluminium nitrate and sulphate are both toxic to plants,
especially clover, when applied in amounts equivalent to the acidity
of the soil. Aluminium oxide and phosphate, on the other hand,
had no effect.[13] It was further found that washing soil with a
solution of potassium sulphate or nitrate removed its acidity, and
also 59 per cent. of its aluminium. The leached soil was better
suited for the growth of clover than the original acid soil. Addi-
tion of lime or calcium phosphate also overcame the acidity and
made the soil fertile. These facts are all consistent with the view
that aluminium is the toxic agent. It is further suggested that
aluminium occurs as gibbsite, a form of aluminium oxide, readily
soluble in acids, which during nitrification or "sulphofication,"
becomes converted into nitrate or sulphate. The weak point in
the suggestion is that neither gibbsite nor other readily soluble
aluminium oxide has commonly been found in soils in temperate
climates, although it must be admitted that they have rarely been
looked for.

An interesting test for sour soils is based on the fact that iron
also, like aluminium, passes into solution when a potassium salt
is added to a sour soil, but not when it is added to a normal
neutral soil. Sourness therefore is readily detected by adding
potassium thiocyanate, and still better by using an alcoholic solu-
tion of this substance.[14]

Soil acidity is now measured by: (1) the lime requirement or
potassium nitrate extraction,[15] essentially titration methods indicat-

[11] See L. P. Howard, *Soil Sci.*, 1919, **8**, 313; *A.*, i, 416.

[12] For further evidence of the chemical origin of soil acidity, see H. A. Noyes,
J. Ind. Eng. Chem., 1919, **11**, 1040; *A.*, i, 211, and R. E. Stephenson, *Soil
Sci.*, 1919, **8**, 41; *A.*, i, 274. For details see E. T. Wherry, *J. Washington
Acad. Sci.*, 1920, **10**, 217; *A.*, ii, 400.

[13] J. J. Mirasol, *Soil Sci.*, 1920, **10**, 153; *A.*, 1921, i, 88.

[14] N. M. Comber, *J. Agric. Sci.*, 1920, **10**, 420.

[15] H. G. Knight, *J. Ind. Eng. Chem.*, 1920, **12**, 340; *A.*, i, 468. For a study
of lime absorption by Indian soils and a method for ascertaining lime require-
ment, see F. J. Warth and M. P. Saw, *Mem. Dept. Agric. India*, 1919, **5**, 157;
A., i, 416.

ing the quantity of the acid; (2) the hydrogen-ion concentration (Sörensen's P_H notation is commonly used),[16] measuring the strength or intensity of the acid. On general grounds one would expect no necessary relationship between these quantities. As a matter of fact, it is now suggested[17] that they may be related, the observed inconsistencies arising from inaccuracies in the Veitch method commonly used in America, or from the presence of "buffers." Seeing, however, that "buffers" occur in all soils it would appear that exceptions would be frequent.

It has sometimes been asserted that the acidity of soil is too feeble to cause injury to plants, and the cause of the infertility must be sought elsewhere.

A set of measurements made in West Virginia[18] give the following optimum P_H values when phosphoric acid and sodium hydrate are the adjusting substances: seedlings of wheat, soja beans and lucerne, 5·94; seedlings of maize, 5·16. In more strongly acid solutions of soja beans and wheat suffered little until the value fell below 5·16; although lucerne suffered at once, 2·96 seems to be below the critical value, and 2·16 was fatal to growth (although not to germination) and favoured the growth of moulds in the cultures. Some injury was observed when the neutral point was attained and considerable injury when it was passed; alkalinity apparently is more harmful than acidity. Other measurements have been made with lucerne at New Jersey, sulphuric acid and calcium carbonate being here the adjusting substances. Germination was practically unaffected between P_H values 4·5 to 7·0; below 4·5, however, it was much retarded.[19] The yield showed a steady increase between P_H values 3·8 to 6·5, with some irregularities between 6·5 and 8. More measurements of this kind are needed; these results suggest slight acidity as the optimum condition, whereas long agricultural tradition favours neutrality attained by use of chalk or lime.

There is one case, however, where slight acidity is known to be desirable—the potato crop, which becomes liable to "scab" if the P_H value is too high. Gillespie gave 5·2 as the limiting value; a case is now known, however, where "scabbing" occurred at 4·8, although it was much reduced in comparison with the control plot at 5·6.[20] Acidification had been brought about by the addition of sulphur, which oxidises in the soil to form sulphuric acid. This method of controlling soil reaction promises to be of much interest.

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[16] The student will find a full account of this method and a critical discussion by E. A. Fisher in *J. Agric. Sci.*, 1920, **11**, 19.

[17] A. W. Blair and A. L. Prince, *Soil Sci.*, 1920, **10**, 253.

[18] R. M. Salter and T. C. McIlvaine, *J. Agric. Res.*, 1920, **19**, 73.

[19] J. S. Joffe, *Soil Sci.*, 1920, **10**, 301.　　[20] W. H. Martin, *ibid.*, 1920, **9**, 393.

Attempts have been made to ascertain in what way the acidity injures plants. The acidity of the sap corresponds with values 5·48 to 5·97 in buckwheat seedlings, and 4·82 in the adult plant;[21] there is also considerable reserve acidity.

These figures may be of the same order as those for optimum conditions in the soil. Some of the results lend colour to the suggestion[22] that the harmful effect of soil acidity exceeding these values is due to its influence in preventing plants from securing rapidly enough the bases necessary for neutralisation and precipitation of acids within the plant; in general, also, the addition of lime to the soil decreases the acidity of the plant juice.

The present position cannot be better described than in the words of D. R. Hoagland,[23] one of the foremost investigators of the modern aspects of soil problems:

" In perhaps the majority of cases the inhibition of crop growth frequently associated with acid soils may not be the direct effect of the acidity at all. In other factors, such as soluble aluminium, may be found the true direct cause of the injury. It is granted that these causes may be removed by exactly the same treatment which neutralises the acidity, but in the interest of scientific progress it is essential to separate and designate the various factors and their inter-relations.

" Is it not possible that the whole subject would become clarified if we attempted to reach such definite conclusions as: ' The growth of the crop is inhibited by too great concentration of hydrogen ion, or by too large a concentration of aluminium ion, or by too low a level of calcium in the soil solution, or by the effect of the hydrogen-ion concentration on the soil micro-organisms, etc.' ? "

Methods of Increasing the Stock of Organic Matter in the Soil.

Considerable attention has been given to green manuring as a means of increasing the supplies of organic matter in the soil. Emphasis has again been laid on the value of leguminous crops, and some precise data have been accumulated.[24] Attempts (unfortunately not giving very definite results) have also been made to ascertain whether or not soil acidity is increased thereby.[25] Further evidence is published that in Virginia, as elsewhere, the growing crop temporarily restricts nitrification in soil, soja beans being an exception.[26]

[21] A. R. C. Haas, *Soil Sci.*, 1920, **9**, 341.
[22] E. Truog, *ibid.*, 1918, **5**, 169.   [23] *Private communication.*
[24] T. L. Lyon, J. A. Bizzell, and B. D. Wilson, *Soil Sci.*, 1920, **9**, 53.
[25] L. P. Howard, *ibid.*, 27.   [26] R. C. Wright, *ibid.*, 1920, **10**, 259.

Soil Organisms.

The effectiveness of leguminous crops arises from the fact that they are associated with micro-organisms capable of fixing gaseous nitrogen and converting it into substances available for the nitrogenous nutrition of the plant. These remarkable organisms have been the subject of much investigation; a life-cycle has been suggested,[27] for which there is considerable evidence. Five stages are described: a small non-motile form, a larger non-motile coccus, an elliptical highly motile form (this being the swarmer stage of Beijerinck), a rod form, and finally, when the carbohydrate supply is exhausted, a vacuolated stage. A neutral reaction and the presence of calcium phosphate speed up the change from non-motile to motile forms. This work is being continued.

Some interesting work on the general biological relationships is being done in Professor A. L. Whiting's laboratory in Illinois. The process of nitrogen fixation was not adversely affected by nitrate or by organic matter; indeed, in the case of cow peas there was some evidence that the addition of organic matter increased it.[28]

Another important practical problem has been studied: whether the organisms are the same for all leguminous plants or whether there are special strains for each kind. Some degree of specificity is proved: the organism of lima bean (*Phaseolus limatus*) is identical with that of cow pea and will inoculate either crop, but it is distinct from that of navy and kidney beans (*Phaseolus vulgaris*), and will not inoculate these.[29]

Nitrates have a marked effect on nodule production. Soja beans take up these compounds readily from the soil; indeed, the concentration of nitrate in the cell sap becomes greater than in the soil solution, and so high as to inhibit growth and reproduction of the organism there.[30]

In addition to the fixation of nitrogen, bacteria play an important part in breaking down the protein contained in plant residues and producing nitrates needed for plant nutrition. Further data have been collected in New Jersey showing that the productiveness is closely related to the rate of evolution of carbon dioxide (described as " oxidising power "), and to a less extent to rate of nitrate accumulation and bacterial numbers.[31]

In a suggestive paper, which may foreshadow important develop-

[27] W. F. Bewley and H. B. Hutchinson, *J. Agric. Sci.*, 1920, **10**, 144.
[28] W. A. Albrecht, *Soil Sci.*, 1920, **9**, 275.
[29] A. L. Whiting and R. Hansen, *ibid.*, 1920, **10**, 291.
[30] W. H. Strowd, *ibid.*, 343.   [31] J. R. Neller, *ibid.*, 29.

ments, Gillespie draws a distinction between oxidations of high potential and those of low potential in a soil.[32] A given rate of absorption of oxygen or production of carbon dioxide may arise from an oxidation of high intensity or potential involving a small quantity of material, or a reaction of low potential involving much material. The phenomena are parallel to those of the hydrogen-ion concentration, and simultaneous development of both aspects of the subject may be expected.

Further work has been done on the protozoan fauna of the soil, and at last it appears that this subject is being put on a sound basis. The method of estimating the numbers of protozoa in natural soils has been greatly improved by D. W. Cutler at Rothamsted;[33] active forms can now be distinguished from cysts and separated out into a number of different species. The first systematic census [34] was taken at intervals of ten days, and the results when plotted, whilst definitely indicating certain relationships, showed many fluctuations which were difficult to understand. A daily count of the organisms in a field plot was therefore organised, and it revealed some remarkably interesting phenomena. The numbers of bacteria were always inversely proportional to the numbers of active amoebæ, whilst the numbers of flagellates showed a remarkable periodicity which is not yet explained. The results [35] are so important that the daily census is being continued for 365 consecutive days. American investigators have sometimes claimed that protozoa were absent or unimportant in American soils, which if true would indicate a great difference in micro-organic flora in this country and America. Using a less complete method of counting, it is now recognised that in the soil of New Jersey there is a fauna of organisms "which are practically always present in the soil in considerable numbers and which use the soil as a medium in which to live and carry on their life processes." The fauna, however, is believed to exist mainly in the non-trophic state.[36] It seems highly desirable that an extended quantitative survey should be made in at least as comprehensive a manner as is done at Rothamsted, discriminating carefully between active forms and cysts; there appears to be no simple direct method of doing this short of actual counts.

Advances in soil microbiology have shown that the soil population is more complex than was at one time thought, but it is also known that some degree of simplification often increases productive-

[32] L. J. Gillespie, *Soil Sci.*, 1920, **9**, 199.

[33] *J. Agric. Sci.*, 1920, **10**, 135.   [34] L. M. Crump, *ibid.*, 182.

[35] D. W. Cutler and L. M. Crump, *Annals of Applied Biol.*, 1920, **7**, 11.

[36] C. R. Fellers and F. E. Allison, *Soil Sci.*, 1920, **9**, 1.

ness. Simplification is obviously advantageous when disease organisms or pests are present. Some organisms tend normally to disappear in the general competition; the *Pseudomonas citri* causing citrus canker in America is rapidly exterminated from ordinary soil, although it flourishes in sterilised soil.[37] In other cases, however, competition alone is insufficient and direct control is attempted. Heat is found to be effective, but its application is rarely feasible. Recourse is therefore had to chemical methods, and substances are sought which, whilst toxic to the organism in question, will not injure the plant. This necessary limitation rules out most inorganic poisons, such as arsenic compounds, mercury salts, etc., and restricts investigators to organic substances. Applications to the soil of calcium sulphide and naphthalene or cymene lead to much increase in the crop and also in numbers of *B. butyricus*, although on fallow soils this particular anaerobic organism does not develop, but there is a loss of nitrogen.[38] In seeking for new agents the first step is to ascertain the effect of various groupings on toxicity. In the case of the wireworm[39] aromatic compounds are more toxic than aliphatic compounds, and the toxicity is successfully increased by the addition of methyl (the least effective), halogen, hydroxyl, or methylamino-groups (most effective). Substitution in the side-chain is more effective than in the ring. The effect is not additive, however; position and other groups both exert great influence. The association of chlorine and nitro-groups is particularly potent, and chloropicrin is one of the most lethal agents tested. In series of compounds of the same chemical type there is a fairly close relationship between toxicity and vapour pressure, rate of evaporation and volatility, toxicity increasing as the volatility decreases, until finally, a limit is reached when the vapour pressure sinks too low to allow of the attainment of a toxic concentration.

Somewhat similar, although less extensive data, are recorded with *Paramoecium*.[40]

A substance highly toxic to the organism, however, will not necessarily suppress it in the soil, as the soil population includes organisms able to effect remarkable decompositions, for example, to break down such unlikely substances as phenol, cresol, and apparently even naphthalene and more stable ring compounds. Owing

[37] H. A. Lee, *J. Agric. Sci.*, 1920, **19**, 189; H. R. Fulton, *ibid.*, 207.

[38] G. Truffaut and N. Bezssonoff, *Compt. rend.*, 1920, **171**, 268 ; *A.*, i, 655.

[39] F. Tattersfield and A. W. R. Roberts, *J. Agric. Sci.*, 1920, **10**, 199. Among possible agents, trichloroethylene deserves consideration: E. Salkowski, *Biochem. Zeitsch.*, 1920, **107**, 191 ; *A.*, i., 794, shows that it is cheap, volatile, and effective. .

[40] N. McCleland and R. A. Peters, *J. Physiol.*, 1919, **53**, xii, xv ; *A.*, i, 512.

to the smallness of the amounts involved and the complex nature of soil, it is difficult to ascertain the course of the decomposition, but some help may be obtained from the work of chemists on the catalytic oxidation of simple but stable organic compounds.[41]

The case of vanillin has been studied in some detail.[42] This substance has been isolated from soil,[43] and it is toxic to plants; it is, however, decomposed by certain soil bacteria. Apparently only a limited number of organisms have this power. It is obvious that micro-organisms capable of breaking down potential plant toxins are of importance in soil fertility.

A further unexpected change apparently brought about by bacteria is the oxidation of the element sulphur when added to the soil. This was first demonstrated in 1916,[44] and was turned to practical account in the conversion of mineral phosphates into soluble phosphate in compost heaps or in the soil. Further details are now worked out, and it is shown that nitrification still proceeds in spite of the formation of acid.[45]

An interesting observation has been made in Egypt to the effect that the fallow or "sheraqi" is a period of biological inactivity in the soil, but is followed by a period of increased activity, the phenomena being apparently parallel to those shown during partial sterilisation of the soil.[46]

In some cases, probably in many, a reaction is brought about by a chain of agencies, chemical and biological. Thus, calcium cyanamide is a well-known fertiliser, but it owes its effectiveness to the ammonia produced in its decomposition. The first stage is the production of carbamide; this is apparently non-biological, since it occurs even after the soil is heated to 135°; the decomposing agent is not yet identified, although the change can be brought about by certain zeolites which may occur in soil. The second stage is the formation of ammonia from the carbamide; this is biological and can be effected by numerous micro-organisms.[47]

An improved method of determining ammonia in soil has been developed.[48]

[41] For example, paraffins: A. Grün, *Ber.*, 1920, **53**, [B], 987; *A.*, i, 518; benzene: J. M. Weiss and C. R. Downs, *J. Ind. Eng. Chem.*, 1920, **12**, 228; *A.*, i, 426.

[42] W. J. Robbins and E. C. Lathrop, *Soil Sci.*, 1919, **7**, 475; *A.*, i, 265; W. J. Robbins and A. B. Massey, *ibid.*, 1920, **10**, 237; *A.*, i, 913.

[43] E. C. Shorey, *J. Agric. Res.*, 1914, **1**, 357; *A.*, 1914, i, 916.

[44] J. G. Lipman, H. C. McLean, and H. C. Lint, *Soil Sci.*, 1916, **2**, 499. For bibliography, see H. C. McLean, *ibid.*, 1918, **5**, 251.

[45] O. M. Shedd, *J. Agric. Res.*, 1919, **18**, 329.

[46] J. A. Prescott, *J. Agric. Sci.*, 1920, **10**, 177.

[47] G. A. Cowie, *ibid.*, 163; *A.*, i, 655.   [48] D. J. Matthews, *ibid.*, 72.

The effect of water supply on bacterial activity has been studied and some useful curves have been drawn; relationships have also been traced with some of the Brigg's and Hilgard's constants.[49]

Relation of Soils to Plant Growth: Water Supply.

One of the most important functions of the soil is to supply water to the plant. This problem has been extensively studied by Livingstone, and he now contributes an important suggestion that may help materially in elucidating the very complex phenomena concerned.[50] The fundamental conception is to regard the soil as a machine delivering water to the absorbing surface of the plant roots; the purpose of the investigation is to study the water-supplying power of the soil. The problem is regarded dynamically, although, of course, it depends on a number of static conditions, such as sizes, kinds, and arrangement of the soil particles, and the water content per unit volume. The experimental method consists in embedding porous porcelain cones in the soil, then after a suitable time withdrawing them and weighing to measure the absorbed water. Special attention is paid to the region of moisture contents where wilting occurs. It appeared from the data obtained (although the authors frankly recognise their preliminary nature) that the water-supplying power at the wilting point was approximately the same for all the twelve soils examined. This critical value is, of course, not to be regarded as a constant for all kinds of plants and all degrees of evaporation, any more than is the wilting coefficient of Briggs and Shantz, which varies in a regular and predictable way for any given soil and plant with the evaporating power of the air.[51] If further investigation confirms the view that the value is independent of the physical make-up of the soil and is the same for sand, loam and humus, it will undoubtedly prove of importance.

The power to supply water, however, is dependent on the amount present, and this is the balance of gains over losses. The loss of water from the soil takes place partly by drainage and partly by evaporation. It is claimed that the rate of evaporation is diminished on addition of soluble salts, and the diminution is directly related to the osmotic concentration of the soil solution.[52]

The water relationships for soils are very complex, and a valuable critical résumé of the whole subject has been made by Keen.[53]

[49] J. E. Greaves and E. G. Carter, *Soil Sci.*, 1920, **10**, 361.

[50] B. E. Livingstone and R. Koketsu, *ibid.*, 1920, **9**, 469.

[51] J. S. Caldwell: The relation of environmental conditions to the phenomenon of permanent wilting in plants, *Physiol. Res.*, 1913, **1**, 1.

[52] M. I. Wolkoff, *Soil Sci.*, 1920, **9**, 409; *A.*, i, 803.

[53] B. A. Keen, *J. Agric. Sci.*, 1920, **10**, 44.

An attempt has also been made to analyse more closely the capillary movement of water through soil.[54]

An important factor, determining not only water supply, but tilth, ease of working the soil, and other properties, is the degree of flocculation of the finer particles. In practice, lime is used to effect this change, but the phenomena do not altogether fall in line with those ordinarily observed with colloids. Some of the apparent contradictions are elucidated in a very suggestive paper by Comber. "Silt," the fine but not the finest material in the soil, is most easily flocculated by calcium salts when the suspension is neutral; this is the usual behaviour of insoluble substances. On the other hand, "clay," the finest material, is most easily flocculated in alkaline suspensions. This is unusual for insoluble substances, but is shown by silicic acid and some of the so-called "emulsoid" colloids. It is suggested that clay as an emulsoid protects the larger particles, which by themselves are suspensoid, and causes the whole soil to be flocculated by lime. In absence of clay, however, lime does not effect flocculation.[55]

Alkali Soils.

Under conditions of low rainfall, salts of sodium may accumulate in soils and produce sodium carbonate by various interactions, which are not yet fully understood.[56] It is suggested that the sulphate may in some cases be reduced to sulphide, which is then decomposed by carbon dioxide to form the carbonate.[57]

However they are formed in the soil, the harmful effects of sodium carbonate, sodium chloride, and other salts on plants and on organisms causing ammonification and nitrification are overcome by the addition of calcium sulphate. In the case of micro-organisms, ferric chloride and sulphate are also effective.[58]

Doubt is now thrown on the current values for the toxicity of these salts in soils. It is shown that soil absorbs more water from a solution of sodium carbonate than from an equivalent solution of sodium chloride, and therefore, under conditions apparently comparable, the plant root would be in contact with a more concentrated solution of carbonate than of the chloride. This fact is said to have been overlooked, and to have

[54] W. Gardner, Soil Sci., 1920, 10, 103, 357.

[55] N. M. Comber, J. Agric. Sci., 1920, 10, 425. For other experiments, see O. M. Smith, J. Amer. Chem. Soc., 1920, 42, 460; A., ii, 296.

[56] For a recent discussion, see A. de Dominicis, Staz. sper. agr. Ital., 1918, 51, 103; A., i, 414.

[57] E. Pozzi-Escot, Bull. Soc. chim., 1919, [iv], 25, 614; A., ii, 185.

[58] J. E. Greaves, Soil Sci., 1920, 10, 77.

led to false conclusions as to the relative toxicity of these substances.[59]

Other Investigations.

Further experiments are reported showing that calcium sulphate increases the amount of soluble matter in soils.[60] The amount of water-soluble material in the soil is not greatly affected by normal variations from the mean moisture content, but it is reduced when air-dry or water-logged conditions are attained.[61]

Work on the drift soil of the Craibstone Farm has been continued.[62] This soil is largely composed of disintegrated granite. Like other soils, it has a marked power of absorbing ammonia, and the property is not shown by all constituents alike, but chiefly by the finer fractions. Powdered granite shows similar powers of absorption. It is not necessary to assume, therefore, that absorption is effected only by decomposed material. Absorption is decreased after ignition.

Fertilisers.

Following the practice of the previous years, the technical aspects of this part of the subject will be discussed in the Report to the Society of Chemical Industry, and only a few of the papers of scientific interest will be referred to here.

Two summaries of long-continued field experiments have been issued. In the New Jersey experiments, the best results were given by sodium nitrate on the unlimed, and ammonium sulphate on the limed, plots, whilst the organic manures (dried fish, dried blood, and tankage) were less effective. No more than one-third of the added nitrogen was recovered in the crop, and, in absence of leguminous plants, there was no accumulation of nitrogen in the soil, but, on the contrary, a loss.[63] In the Ohio experiments summarised by Director Thorne, very similar results were obtained; sodium nitrate proved better than ammonium sulphate on unlimed, but not on limed, soils, and both proved better than tankage.[64] One case is reported, however, where an organic manure proved more effective than others, namely, that of the American "blueberry." Sodium nitrate by itself somewhat depressed the yield;

[59] T. H. Kearney, *Soil Sci.*, 1920, **9**, 267; *A.*, i, 588.
[60] M. M. McCool and C. E. Millar, *J. Agric. Res.*, 1920, **19**, 47; *A.*, i, 588.
[61] J. C. Martin and A. W. Christie, *ibid.*, 1919, **18**, 139.
[62] W. G. Ogg and J. Hendrick, *ibid.*, 1920, **10**, 333, 343.
[63] J. G. Lipman and A. W. Blair, *Soil Sci.*, 1920, **9**, 371.
[64] C. E. Thorne, *ibid.*, 487.

complete artificial manure somewhat increased it, but a mixture of the latter and dried blood considerably increased it. The manuring of fruit has, however, always been a subject of some difficulty, bristling with exceptions to all the rules.[65]

In all fertiliser work, it is necessary to carry out field trials, and, in spite of their apparent simplicity, they are liable to many sources of error. A useful summary has been prepared of the methods by which the more serious errors can be avoided, special stress being laid on Larsen's method.[66]

The effect of magnesium carbonate on plant growth is a subject of much practical importance; a persistent idea is current among practical men that it is in some way harmful to crops, and, in consequence, magnesium limestone is not held in high repute. Many experiments have been made. Recently, in Indiana, magnesite proved more favourable than calcite for nitrification and for multiplication of aerobic and anaerobic bacteria on a yellow clay soil, but not on a black soil; it produced a greater increase in soluble salts in the soil, and led to larger increases in yield of beet, but smaller increases of wheat and clover, than did calcite.[67] On the other hand, it is claimed that full crops are not obtainable on soils where magnesia is in excess of lime.[68]

Plant Growth.

The nutrient salts absorbed by plants from soil, together with the carbon dioxide assimilated by their leaves, are elaborated into the complex constituents and contents of the plant cells. The processes involved continue to form the subject of much investigation. The relationships between absorption of salts by the plant root and composition of the nutrient medium is being studied at the California Experimental Station, where, in the case of barley, three distinct phases in the absorption of the nutrients were found.[69] Up to the time of formation of the head, the rate of absorption progressively increases until, finally, the amounts of nitrogen and of potassium reach a maximum. The second phase corresponds with the translocation of material into the developing heads; this is marked, not only by a decreased rate of absorption from the soil, but by definite and substantial losses of nitrogen, potassium, and apparently calcium from the aerial parts of the

[65] C. S. Beckwith, *Soil Sci.*, 1920, **10**, 309.
[66] J. Sebelien, *J. Agric. Sci.*, 1920, **10**, 415.
[67] S. D. Corner and H. A. Noyes, *J. Agric. Res.*, 1919, **18**, 119.
[68] J. Hughes, *J. Bath and W. and S. Co. Soc.*, 1919, [v], **13**; *A.*, i, 416.
[69] J. S. Burd, *J. Agric. Res.*, 1919, **18**, 61.

plant, and presumably from the whole plant, although difficulties of manipulation make root examination uncertain. Towards the end of the period, the lost materials are regained. The final stage is ripening, during which absorption ceases and losses are resumed. It is suggested that these movements of salts into and out from the plant may be due to purely physical causes, as low concentration of the water extract of the soil occurs simultaneously with the movement out from the plant. The results suggest that the normal relationship between plant and soil is to have a relatively high soil concentration in the early stages of growth and a low concentration in later stages.

Reference has been made in earlier Reports to the work of Shive and Tottingham, in which it is claimed that plants need not only an adequate supply of various nutrient substances, but also some kind of relationship or "physiological balance" between the particular elements. The data show considerable variations, but the ratio of nutrients causing maximum growth is called the optimum ratio. This ratio is found to alter with the concentration of the nutrient solution; it is not the same at 0·1, 1·75, and 4 atmospheres,[70] but it is unaffected by the nature of the medium, being the same in sand as in water culture. So also it is independent of variations in the moisture content of the sand, and is the same for degrees of moistness varying from 40, 60, to 80 per cent. of the water-retaining capacity of the sand. It is not, however, constant for the whole range of growth of the plant, being different in seedling and adult stages, and different for the growth of "top" and of the roots.

Closely associated with this conception of physiological balance is that of antagonistic action between ions. Wheat seedlings are adversely affected by sodium chloride and sodium sulphate, but the toxic effects are largely overcome by small amounts of calcium oxide or calcium sulphate, and to a less extent by magnesium sulphate and barium chloride. The lime did not prevent the entrance of the sodium salts into the plant; its antagonistic effect was therefore not attributable to any reduction of permeability.[71]

Calcium salts also enable the plant to overcome the harmful effects of copper salts, although they do not prevent the entry of copper into the plant. It is considered more probable that the calcium favours the evolution of the plant, giving it greater vigour, and in particular greater volume, into which the copper diffuses, thus preventing dangerous accumulation in any one region.[72]

[70] J. W. Shive, *J. Agric. Res.*, 1920, **18**, 357.
[71] J. A. LeClerc and J. F. Breazeale, *ibid.*, 347; *A.*, i, 413.
[72] L. Maquenne and E. Demoussy, *Compt. rend.*, 1920, **170**, 420; *A.*, i, 357.

Attention has, however, been directed to the possibility that certain ions may alter the plasma colloids [73] or the permeability of the plant cells.[74] Ferrous salts are known to be more injurious to young plants than ferric salts, and therefore any condition which favours their oxidation reduces the toxic effects. It is shown that monopotassium phosphate and copper sulphate both have this effect.[75] Neither manganese sulphate nor chromium salts were found effective as fertilisers.[76]

The functions of the various nutritive elements are determined indirectly. Some work has been done this year on calcium.[77] There seems to be a close relationship between the calcium and nitrogen content of plants, and the more important crops can be divided into two groups: (a) those with low content of calcium and nitrogen, a low calcium–nitrogen ratio, and low lime requirements; (b) those with high content of calcium and nitrogen, high ratio, and high lime requirement. It is suggested that protein metabolism is probably one of the chief sources of plant acids, and may give rise to the need for calcium.

The question whether silicon is necessary for plant nutrition has been raised. An artificial calcium silicate was tested against calcium carbonate, and found to be in no way superior. It appears, therefore, that silicon in this compound is of no advantage to the growing crop.[78]

An interesting and entirely novel suggestion as to the function of potassium in plants has been brought forward. It is claimed[79] that the potassium ion may, as regards function, be replaced by all the other radioactive elements, heavy or light, provided the doses are equiradioactive; it may also be replaced by a free radioactive radiation.

Some attention has been given to the action of copper salts on vegetation. It is shown that copper is a frequent, and possibly a normal, constituent of plants.[80] It is claimed, in spite of

[73] T. Tadokoro, *J. Coll. Agr. Hokkaido. Imp. Univ., Sapporo, Japan*, 1919, 8, 143; *A.*, i, 585; S. M. Neuschlosz, *Pflüger's Archiv*, 1920, 181, 17; *A.*, i, 698.

[74] O. L. Raber, *J. gen. Physiol.*, 1920, 2, 535, 541; *A.*, i, 585, 586.

[75] L. Maquenne and E. Demoussy, *Compt. rend.*, 1920, 171, 218; *A.*, i, 654.

[76] T. Pfeiffer, W. Simmermacher, and A. Rippel, *Fühlings Landw. Zeit.*, 1918, 313; *A.*, i, 652; F. Weis, *K. Vet.-Landbohöjskole Aarsskrift*, 1919, 239; *A.*, i, 652.

[77] F. W. Parker and E. Truog, *Soil Sci.*, 1920, 10, 49; *A.*, i, 702.

[78] B. L. Hartwell and F. R. Pember, *ibid.*, 57.

[79] H. Zwaardemaker, *J. Physiol.*, 1920, 53, 273; *A.*, i, 511; *Pflüger's Archiv*, 1918, 173, 28; *A.*, i, 345.

[80] E. Fleurent and L. Lévi, *Bull. Soc. chim.*, 1920, [iv], 27, 440, 441; *A.*, i, 584.

previous work to the contrary, that dilute solutions of copper sulphate added to water cultures have a favourable action on the growth of roots and stems of peas and wheat.[81]

Theoretical discussions have been attempted [82] of the physico-chemical basis of the phenomena of absorption and elaboration of nutrient salts, and of the effects of these salts on cell division.[83]

For many years it was supposed that nitrates, phosphates, and simple salts of potassium, calcium, magnesium, etc., were alone necessary to plant growth, no organic compound of any kind being required. Recently it has been asserted that certain organic compounds are helpful, if not necessary, and lead to marked increases in growth. The case of *Lemna major* has been studied in London; crude nucleic acid derivatives from bacterised peat, the growth products from *Azotobacter chrococcum* and *Bacillus radicicola*, leaf mould, fresh and well-rotted stable manure, and well-manured fertile soil all contained water-soluble substances which promoted the growth of this organism.[84] In California, dilute extracts of peat (10 parts in 1,000,000 of water) produced a marked stimulation of root growth of citrus seedlings,[85] which could not be obtained with corresponding solutions of sodium nitrate or potassium chloride. On the other hand, bouillon prepared from fresh brewers' yeast, which had been heated to 135° and rendered incapable of curing polyneuritis in pigeons, was still effective in improving the growth of fungi.[86]

Assimilation.—The ease and rapidity with which the plant in sunlight absorbs carbon dioxide and converts it into sugar has always been a source of wonder to chemists, who have never yet been able to reconstruct the process.

Support is periodically forthcoming for Baeyer's old hypothesis; it is claimed [87] that formaldehyde can be absorbed by plant leaves and transformed into plant tissue. There are, however, difficulties in the way of this hypothesis, and another has been put forward, which is claimed to be more in accordance with the facts. The first stage is supposed to be the isomerisation of carbon dioxide, with the formation of a secondary peroxide, $>C<^{O\cdot OH}_{OH}$; this

[81] L. Maquenne and E. Demoussy, *Compt. rend.*, 1920, **170**, 1542; *A.*, i, 584.

[82] E. Reinau, *Zeitsch. Elektrochem.*, 1920, **26**, 329; *A.*, i, 799.

[83] J. Spek, *Koll. Chem. Beihefte*, 1920, **12**, 1; *A.*, i, 353.

[84] W. B. Bottomley, *Proc. Roy. Soc.*, 1920, [B], **91**, 83; *A.*, i, 265; F. A. Mockeridge, *Biochem. J.*, 1920, **14**, 432; *A.*, i, 704.

[85] J. F. Breazeale, *J. Agric. Res.*, 1919, **18**, 267.

[86] A. Lumière, *Compt. rend.*, 1920, **171**, 271; *A.*, i, 652.

[87] M. Jacoby, *Biochem Zeitsch.*, 1919, **101**, 1; *A.*, i, 800.

eliminates oxygen and yields the group $>C<^H_{OH}$, which is predisposed towards condensation. Chlorophyll is assumed to sensitise the preliminary isomerisation and to act as catalyst in the final condensation.[88]

Another hypothesis[89] is that the carbon dioxide polymerises to form tetrahydroxyethylene, and this passes over into the keto-form:

$$O{=}C{=}O \atop O{=}C{=}O \quad {+2H_2} \quad \bigg| O \rightarrow \begin{array}{c} HO{-}C{-}OH \\ \parallel \\ HO{-}C{-}OH \end{array} \rightarrow \begin{array}{c} H \\ O{-}C{-}OH \\ \diagdown \\ HO{-}C{-}O \\ H \end{array} \bigg| {+O_2}$$
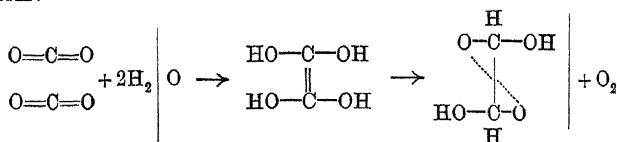
which contains the characteristic sugar grouping $HO{-}\underset{|\quad|}{C}{-}O$.

The formation of plant acids, sugars, etc., is easily deduced.

Some of the physical phenomena associated with the process have been investigated; the effect of various factors on its velocity,[90] and the fact that colloidal chlorophyll is much more sensitive to light than the natural product, although the sensitiveness can be depressed by various agents[91]; and the fluorescent phenomena studied by the spectroscope.[92]

The process has also been discussed from the point of view of its dependence on the internal pressure of carbon dioxide in plants.[93] A simpler form of apparatus for the study of photosynthesis has been described.[94]

From time to time it has been suggested that the growth of plants ought to be increased by additions of carbon dioxide to the atmosphere, and some instances of increase so obtained in a glasshouse are given.[95] Field applications of this method may not be feasible, but under glass there may be possibilities worth investigating.

It is usually supposed that nitrogen is necessarily assimilated in the form of some simple compound, such as nitrate, ammonia, or

[88] G. Woker, *Pflüger's Archiv*, 1919, **176**, 11; *A.*, i, 354.

[89] P. R. Kögel, *Zeitsch. wiss. Photochem.*, 1920, **19**, 215; *A.*, i, 355.

[90] O. Warburg, *Biochem. Zeitsch.*, 1919, **100**, 230; 1920, **103**, 188; *A.*, i, 583, 798.

[91] R. Wurmser, *Compt. rend. Soc. Biol.*, 1920, **83**, 437; *A.*, i, 560.

[92] K. Stern, *Ber. Deut. bot. Ges.*, 1920, **38**, 28; *A.*, i, 700.

[93] E. Reinau, *Chem. Zeit.*, 1919, **43**, 339; *A.*, i, 128.

[94] W. J. V. Osterhout, *Bot. Gaz.*, 1918, **68**, 60; *A.*, i, 128.

[95] M. B. Cummings and C. H. Jones, *Bull.*, 1919, **211**, 56 pp.; *A.*, i, 267. See also F. Riedel, *Stahl und Eisen*, 1919, **39**, 1497.

carbamide,[96] and it is certainly true that assimilation usually proceeds in this way. Periodically, it has been assumed that gaseous nitrogen might be assimilated by higher plants, but the possibility has not been taken seriously by physiologists. It is known, however, that certain bacteria can effect this assimilation, and from gaseous nitrogen and carbohydrates can synthesise cell proteins; but these bacteria have no power of synthesising carbohydrates: they are dependent on pre-formed sources of these materials. Moore has made the interesting announcement that certain unicellular algæ possess the power of fixing, not only gaseous nitrogen, but carbon also, so that they can by themselves, and without pre-formed carbohydrates, construct the whole organic contents of their cells.[97] If this result is confirmed, it will alter some of the fundamental conceptions of soil microbiology and plant physiology.

The Growth of Plants: Effect of Light and Temperature.— Investigators dealing with the growing plant are soon compelled to realise the dominating effect of factors other than the supply of plant nutrients. One of the most important is light. The rate of growth is directly proportional to the length of the day, and this factor also profoundly affects the sexual reproduction of plants; in many species the flowering and fruiting stages can be attained only when the length of day falls within certain limits, for example, in natural conditions only during certain seasons.[98] In absence of sufficient day length, vegetative growth may continue more or less indefinitely, thus leading to the phenomena of gigantism; or, on the other hand, under the influence of suitable day length, precocious flowering and fruiting may be induced. In some cases, a day length was found suitable both to vegetative growth and reproduction; an ever-blooming or ever-bearing habit was then obtained. By suitable variation of the length of day, it was possible to give annuals a perennial habit, or, on the other hand, to hasten their processes, so that they would go through two cycles of alternate vegetative and reproductive activity in one season. Variations in intensity of light had little effect, the normal intensity, as shown by H. T. Brown, being more than sufficient for the needs of the plant.

Moisture supply and temperature are equally important factors: these have been invoked to explain the stunted growth in wind-

[96] T. Bokorny, *Pflüger's Archiv*, 1918, **172**, 466; *A.*, i, 413, shows that carbamide is utilisable in proper conditions.

[97] B. Moore and T. A. Webster, *Proc. Roy. Soc.*, 1920, [B], **91**, 201; *A.*, i, 466.

[98] W. W. Garner and H. A. Allard, *J. Agric. Res.*, 1920, **18**, 553.

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swept districts, evaporation being so marked that the plant is seriously cooled and deprived of adequate water supply. When these factors are made good, wind does little harm to crop growth.[99]

Of the numerous specialised papers, two may be mentioned. It is shown that cereal seeds can withstand dry heat to a temperature of 100° for some hours without serious loss of germinating power, whilst some of the disease spores affecting seeds were killed.[1]

Studies have been made on somewhat similar lines of wilt-producing fungi, temperature having been found which will keep them in check without unduly damaging the plant.[2]

Composition of Crops.

Few problems present greater difficulty than those associated with the composition of crops. Farmers grow crops in order to sell them, but neither they nor the purchasers know what is in them. Little is known of the composition of crops, and, unfortunately, it is proving very difficult to arouse any interest in this or the closely allied subject of quality in crops.

The oat crop is one of the most important to the farmer, and it has been studied in detail by Berry at the West of Scotland Agricultural College.[3] A mass of analytical data is presented which is by far the most extensive hitherto available in this country. Various relationships were found between weight and composition of the kernel; with the thin, husked, white grains, as the kernel increased in weight the proportion of husk decreased, the oil and fibre diminished, whilst the carbohydrates, the yield of grain, and the proportion of grain to total produce increased. It is an important practical observation that the yield per acre is associated directly with the average size of individual grains, whilst the production of straw varies in the opposite direction.

The composition of the grain was affected by variation in organic matter content of the soil, for example, ploughed-up grassland and arable land, but season produced comparatively little effect, and artificial fertilisers still less. Locality, however, had a marked effect.

Investigations on the wheat crop on somewhat similar lines have been made at the University of Manitoba.[4] In an important paper it is shown that the protein content of wheat is much affected by climatic factors, by restriction of water supply, and by varietal

[99] L. Hill, *Proc. Roy. Soc.*, 1921, [B], **92**, 28.

[1] D. Atanasoff and A. G. Johnson, *J. Agric. Res.*, 1920, **19**, 379.

[2] H. A. Edson and M. Shapovalov, *ibid.*, **18**, 511.

[3] R. A. Berry, *J. Agric. Sci.*, 1920, **10**, 359.

[4] H. E. Roberts, *J. Agric. Res.*, 1920, **10**, 121.

factors. In breeding new varieties for general purposes, it is suggested that strains should be sought which vary greatly in their protein content, since a wide starch–protein ratio would probably mean greater climatic adaptability. For restricted areas, however, wheats of maximum protein content should be sought. The reduction of protein subsequent on irrigation can be largely counterbalanced by introducing lucerne into the rotation.[5]

Plant Constituents.

Constant additions are being made to the long list of plant constituents, and little more than the briefest reference is possible here. Until the function of a substance is known, the mere fact of its presence is not necessarily of much physiological interest.

Cellulose, Lignin, etc.—These substances constitute the larger portion of the material of the plant structure, and steady progress is being made with the knowledge of their constitution.[6] Perhaps the most important paper on this subject is a critical discussion of the constitution of cellulose.[7] Lignin has also been the subject of investigation; it has received the formula $C_{40}H_{40}O_{11}$, and is supposed to be built up from pentoses.[8]

Plant Pigments.—*Flavones* are yellow pigments; those obtainable from the tulip[9] and from Rhus[10] have been studied.

Anthocyanins are formed from flavones by reduction. The red pigment of the young leaves of the grape vine is regarded as identical with œnidin, the anthocyanidin derived from the pigment of the purple grape. This is the first instance recorded in which the red leaf pigment is an anthocyanidin.[11]

Members of the beet-red group of anthocyanins have been found in the skins of fuchsia and cacti berries, and in the petals of scarlet cactus flowers.[12]

Anthocyanins are further reducible to leuco-bases.

The tinctorial properties of a number of the anthocyanins have been studied.[13]

[5] J. S. Jones, C. S. Cohen, and H. P. Fishburn, *J. Agric. Sci.*, 1920, **10**, 290.

[6] P. Klason, *Arkiv Kem. Min. Geol.*, 1917, 6, No. 15; *A.*, i, 148.

[7] K. Hess and W. Wittelsbach, *Zeitsch. Elektrochem.*, 1920, **26**, 232; *A.*, i, 532.

[8] P. Klason, *Arkiv Kem. Min. Geol.*, 1917, 6, No. 15; *A.*, i, 148.

[9] B. Harrow and W. J. Gies, *Proc. Soc. Expt. Biol. Med.*, 1918, **16**, 8; *A.*, i, 70.

[10] C. E. Sando and H. H. Bartlett, *Amer. J. Bot.*, 1918, **5**, 112; *A.*, i, 272.

[11] O. Rosenheim, *Biochem. J.*, 1920, **14**, 178; *A.*, i, 467.

[12] F. Kryz, *Oesterr. Chem. Zeit.*, 1920, **23**, 55; *A.*, i, 515.

[13] A. E. Everest and A. J. Hall, *J. Soc. Dyers and Col.*, 1919, **35**, 275; *A.*, i, 70.

Sugars and Other Carbohydrates.—An improved method for detecting dextrose in plants has been described.[14] Both gentianose and sucrose have been detected in the roots of *Gentiana cruciata* and *G. purpurea.*[15]

Primeverose has been isolated from *Primula officinalis*; it is a biose formed by combination of a molecule of dextrose and a molecule of xylose, and it has a free aldehyde group.[16]

Inulin is the storage product in some plants, notably the artichoke. It does not occur in the leaves, but is formed in the stem and the tuber, presumably from the dextrorotatory carbohydrates supplied to the leaves.[17]

Odorous Constituents.—The odorous constituents of apples have been found to consist essentially of the amyl esters of formic, acetic, and hexoic acids, with a very small amount of the octoic ester, and, in addition, acetaldehyde, and probably some free acid.[18]

Proteins.—Osborne has continued his work on plant proteins, and has turned to the difficult problem of the leaf proteins, spinach being selected for examination. At least 40 per cent. of the total nitrogen of the leaves was found in the form of colloidal protein, which, however, may be in some form of combination with a substance of pentosan nature. A nearly colourless protein was, however, obtained.[19]

Two globulins and an albumin have been extracted from the Georgia velvet bean.[20] Globulins have been extracted from the coconut (*Cocos nucifera*)[21] and the jackbean (*Canavalia ensiformis*),[22] whilst phaseolin has been studied,[23] and also the proteins of polished rice.[24]

Alkaloids.—Nicotine is not present in the seed of tobacco; it is, indeed, harmful to germination, but it appears in the young plant immediately the chlorophyll begins to function, and it originates in the leaves. In case of injury, for example, cutting, the alkaloid is produced in increased quantity in the adjoining tissues. It is

[14] E. Bourquelot and M. Bridel, *Compt. rend.*, 1920, **170**, 631; *A.*, ii, 337.

[15] M. Bridel, *J. Pharm. Chim.*, 1920, [vii], **21**, 306; *A.*, i, 467.

[16] A. Goris and C. Vischniac, *Compt. rend.*, 1919, **169**, 871, 975; *A.*, i, 14.

[17] H. Colin, *Bull. Assoc. Chim. Sucr.*, 1919, **37**, 121; *A.*, i, 358.

[18] F. B. Power and V. K. Chesnut, *J. Amer. Chem. Soc.*, 1920, **42**, 1509; *A.*, i, 653.

[19] T. B. Osborne and A. J. Wakeman, *J. Biol. Chem.*, 1920, **42**, 1; *A.*, i, 516.

[20] C. O. Johns and H. C. Waterman, *ibid.*, 59; *A.*, i, 515.

[21] C. O. Johns, A. J. Finks, and C. E. F. Gersdorf, *ibid.*, 1919, **37**, 149; *A.*, i, 210. [22] J. B. Sumner, *ibid.*, 137; *A.*, i, 210.

[23] A. J. Finks and C. O. Johns, *ibid.*, 1920, **41**, 375; *A.*, i, 401.

[24] J. Kurosawa, *J. Tokyo Chem. Soc.*, 1919, **40**, 551; *A.*, i, 414.

supposed, therefore, that nicotine is elaborated by the plant from certain residues of the nitrogen katabolism, either to prevent accumulation of these residues or to utilise them with intensification of their harmfulness in defence of its organs.[25]

Lycorine, $C_{16}H_{17}O_4N$, has been found in various plants of the order Amaryllidaceæ.[26]

Hydrogen Cyanide.—Considerable technical importance attaches to the occurrence of hydrogen cyanide in plants. This substance usually occurs in glucosidal combination, as in bitter almonds, cherry laurel leaves, seeds of *Phaseolus lunatus*, etc. It may also occur, however, in non-glucosidal form, in the buds of the cherry laurel and the young leaves of *Sambucus niger.*[27]

Enzymes.—It is not proposed to discuss here the general problem of enzyme activity, but reference must be made to one paper. The peroxydasic function in plants, which appears to be shown by living cells only,[28] and is usually attributed to enzymes, now appears to be due to iron compounds, katabolic products of more complex compounds, such as næmatoids, which, in virtue of their physical state, are able to act between the oxidisable substances and the peroxides.[29]   E. J. RUSSELL.

[25] L. Bernadini, *Atti R. Accad. Lincei*, 1920, [v], **29**, i, 62 ; *A.*, i, 412.

[26] K. Gorter, *Bull. Jard. bot. Buitenzorg*, 1920, [iii], **1**, 352; *A.*, i, 467.

[27] L. Rosenthaler, *Schweiz. Apoth. Zeit.*, 1919, **57**, 571 ; *A.*, i, 271.

[28] J. G. McHargue, *J. Amer. Chem. Soc.*, 1920, **42**, 612 ; *A.*, i, 406.

[29] G. Gola, *Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 146 ; *A.*, i, 208.

CRYSTALLOGRAPHY AND MINERALOGY.

THE striking renewal of activity in the subjects under review in this Report is all the more gratifying because they were among the first to suffer from the outbreak of war. The volume of work to be noted is, indeed, so considerable that space will not allow some investigations to be treated in accordance with their intrinsic merits. This is especially the case perhaps in the province of crystal-structure. In the first place, there are to be noted two books of more than ordinary value. The one by Niggli[1] not only contains a full and clear account of all the point-systems, but also brings the subject up to date in the light of X-ray methods and results. Sommerfeld's book[2] is more general, covering, in fact, recent developments in a wide field of physical discovery and interpretation, to which the study of crystals has contributed so powerfully. Then there are two important contributions to the related subjects of atomic distances and volumes, and also many successful reconstructions of crystals, all of which will receive due notice. On the other hand, an ingenious development of X-ray technique[3] must be disposed of here somewhat summarily. The method depends essentially on the study of a sequence of Laue photographs, the crystal being turned through a known number of degrees, by the help of a special two-circle goniometer, between the various exposures. The photographs are then analysed by the help of a new instrument termed a "cyclometer," and the direction of a structural plane of symmetry, if such be present, is thereby located. Fresh exposures on the goniometer lead to a determination of the "X-ray class of symmetry," that is, the real class to which has been added a centre of symmetry; and a set of crystal-elements can also be deduced. In other words, the investigation can be evidently carried to the same stage as is custom-

[1] P. Niggli, "Geometrische Krystallographie des Diskontinuums," 1919, a book that arose from an analytical investigation of the cubic-point system by the same author, *Jahrb. Min. Beil-Bd.*, 1919, **43**, 1.

[2] A. Sommerfeld, "Atombau und Spektrallinien."

[3] R. Gross, *Centr. Min.*, 1920, 52.

ary by orthodox geometrical methods, but the crystal need have no plane faces. The method has already been applied to crystals of tungsten,[4] and also, without an actual publication of details, to tridymite and hæmoglobin.

What appears to be a final determination of the symmetry-class of the mineral benitoite may well be mentioned here, as illustrating the meaning of the term X-ray class of symmetry. According to F. Rinne,[5] there are only three symmetry-classes which are worthy of a consideration: (1) trigonal equatorial, (2) ditrigonal equatorial, and (3) ditrigonal polar, each of which by addition of a centre of symmetry happens to lead to a distinct class, namely, (1) hexagonal equatorial, (2) dihexagonal equatorial, and (3) dihexagonal alternating. Laue photographs of homogeneous portions of a crystal unmistakably rule out the first and third alternatives, and benitoite is accordingly the first representative of the ditrigonal equatorial class.

Theoretical discussions of the finer details of crystal structure are becoming more frequent. The effect of various possible types of electronic arrangement on the general symmetry of the diamond, rock-salt, and sylvine has been worked out by H. Thirring.[6] With regard to the much-vexed question of the chemical aspect of crystal structure, opinion would seem to have taken a welcome, if belated, turn in the German literature—perhaps on account of Willstätter's[7] expressed opinion that the disappearance of the molecule in a crystal cannot be reconciled with the immense body of well-established facts of organic chemistry. Two papers by A. Reis[8] are also suggestive in this connexion. An allusion may also be made here to the important work, which has been carried on during the last twenty-five years, on the behaviour of crystals to infra-red radiation—work that is disseminated in various journals and worthy of a complete Report in itself. In a sense, the work has more chemical interest than X-ray work, for infra-red radiation would seem to be a molecular as opposed to an atomic probe. All carbonates, for example, exhibit an intense reflection for infra-red rays of a specific wave-length, no matter whether they are in the state of fusion, solution, or crystal. Quite recently there have been numerous attempts to correlate the extreme wave-lengths (residual rays—" Reststrahlen "), selectively reflected by crystals, with the elastic and other constants. An important paper by H. Rubens and H. von Wartenberg[9] is the key to

[4] R. Gross and N. Blassman, *Jahrb. Min. Beil-Bd.*, 1919, **42**, 728.

[5] *Centr. Min.*, 1919, 193.

[6] *Physikal. Zeitsch.*, 1920, **21**, 281; *A.*, ii, 477.

[7] R. Willstätter, *Zeitsch. angew. Chem.*, 1919, **32**, 331.

[8] *Zeitsch. Elektrochem.*, 1920, **26**, 408, 412.

[9] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 189; *A.*, 1914, ii, 236,

some of the earlier papers. Some supplementary references[10] to more recent papers may be useful to those who are interested. It must be noted that the conclusions about fluorspar are vitiated by an arithmetical mistake. An early publication of the new computations is promised.

As the portion devoted to Mineralogy is supposed to cover a period of three years, it will be realised that no space can be allotted to the results of chemical analysis and descriptions of new mineral species; further, that little attention can be devoted to what may be termed the observational side of the science. Fortunately, these aspects are already well cared for in special journals. A recent list of new minerals, for example, has been given by Spencer,[11] and a new venture on the part of the *Mineralogical Magazine*—the publication of abstracts—would seem to be justified by results. Several important American investigations of mineral systems are to be noted, which emphasise the desirability of the foundation on this side of something of the nature of a Petrophysical Institute; which, without being an exact copy of the American original, could fruitfully co-operate with it in the advancement of pure and applied science. Without some such centre there are almost insuperable difficulties in the way of any serious European contributions to experimental mineralogy, for the problems there involved require such special resources as are scarcely within the power of a University laboratory to provide. One department of such an Institute might well be devoted to the manifold chemical problems connected with crystals. The future of crystallo-chemical analysis, in particular, would seem to require something more than the spasmodic support of individuals. The simplification of the method, and the reduction to a unified system of the numerous compounds described within the last six years, not to speak of the limitless compounds of the future, would require some form of organised effort. Chemists could then be encouraged, not only to send their new crystalline compounds to be investigated and registered, but also to expect help, as a matter of course, in the identi-

[10] H. Rubens, *Ber. Deut. physikal. Ges.*, 1915, 17, 315 ; *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1917, 43 ; H. P. Hollnagel, *Physical Rev.*, 1918, 11, 135 ; M. Born, "Dynamik der Kristallgitter," 1915 ; *Ber. Deut. physikal. Ges.*, 1919, 21, 533 ; M. Born and O. Stern, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 48, 901 ; M. Born, *ibid.*, 1918, 604 ; *A.*, ii, 401 ; M. Born and A. Landé, *Ber. Deut. physikal. Ges.*, 1918, 20, 210 ; *A.*, 1919, ii, 188 ; A. Landé, *ibid.*, 1918, 20, 217 ; 1919, 21, 644 ; K. Fajans, *ibid.*, 1919, 21, 539, 714 ; *A.*, ii, 21 ; M. Born, *ibid.*, 1919, 21, 533 ; *Ann. Physik*, 1920, [iv], 61, 87 ; *A.*, ii, 227 ; M. Born and E. Bormann, *ibid.*, 1920, 62, 218 ; W. Voigt, *ibid.*, 1919, 60, 638.

[11] L. J. Spencer, *Min. Mag.*, 1919, 18, 373.

fication of complex products of reaction, especially in those cases in which they are hampered by a paucity of material.

Atomic Distances and Volumes.

Two recent attempts to carry our knowledge of atomic volumes beyond the stage represented by Lothar Meyer's well-known curve would seem to indicate substantial progress towards a solution of the simpler problems connected with this most difficult subject.

The first paper to be noted deals not so much with volumes as with atomic distances in crystals. As a result of a critical survey of the numerous structures which have been successfully determined by various X-ray workers, W. L. Bragg [12] finds that the distance between contiguous atomic centres of any given pair of elements, A and B, is almost constant for all crystals. Now, if the atoms be regarded as spherical, this distance can be regarded as made up of the sum of the radii of the two atoms, and if the radius of atom A be known then the radius of atom B can be obtained by subtraction. In this way, by making use of the X-ray data referring to such crystalline elements as carbon, silicon, and various metals, the author is subsequently able to deduce preliminary values for the atomic radii of such elements as oxygen, nitrogen, sulphur, and the halogens, which have so far only been investigated in the form of compounds. These preliminary estimates are then mutually adjusted by an elaborate series of cross-checks, the result being a table of mean radii or diameters, in agreement as a rule with individual observations within the limits ±10 per cent. Further, it is possible to deduce diameters for certain other elements from comparisons of the molecular volumes of isomorphous substances. The results are given in the form of a curve (with atomic diameters plotted against atomic numbers), which is here reproduced as far as the element strontium (see Fig. 1). It is seen that the diameters, as thus deduced from the established structures of crystalline elements and compounds, are of the same periodic character as the so-called atomic volumes of the Lothar Meyer curve. (Parenthetically, it may be here added that the ionic radii for the halogens and alkali metals have been deduced in another way by A. Landé,[13] who attributes a greater radius to a halogen ion than to an ion of the alkali metal immediately following it in the list of the elements. A similar view is held by K. Fajans.[14] This want of agreement between Bragg and Landé and Fajans cannot be discussed here, as the more important of the German papers are not available.)

[12] *Phil. Mag.*, 1920, [vi], **40**, 169 ; *A.*, ii, 537.

[13] *Zeitsch. Physik*, 1920, **1**, 191 ; *A.*, ii, 540.

[14] *Ibid.*, **2**, 309 ; *Zeitsch. Elektrochem.*, 1920, **26**, 502.

H*

Bragg's paper must be consulted for a discussion of the physical significance assigned to these diameters. The immediate object would seem to be strictly practical. "The way of regarding the atoms as spheres packed tightly together is useful in constructing models of crystalline structures . . . and, it is hoped, will help in future investigations . . . by limiting the number of possible arrangements." An example of this practical usefulness will be given below under cæsium dichloroiodide. The writer would also mention that the application of the method to the cassiterite group and to anatase[15] points to the need of a revision of the models which have hitherto been offered.

The second investigation refers to the volumes of elementary atoms. Setting out from the current view that the elements typified by sodium, magnesium, aluminium, and silicon respectively possess 1, 2, 3, and 4 outer electrons, and a corresponding effective

Fig. 1.
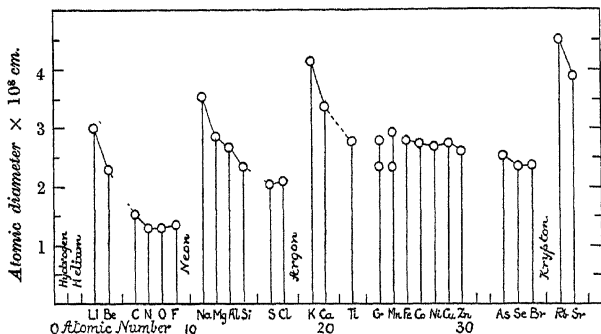
number of positive charges on the nucleus, Sommerfeld[16] examines the attractive effects of these successive increases in nuclear charge on the radius of the outer electronic ring, and he deduces that the atomic radii of the four elements specified should exhibit the ratios $1:0.57:0.42:0.33$. He also points out (as will be indicated presently) that these values are in fair agreement with the values obtained by dividing atomic weight by specific gravity. Now W. L. Bragg has emphasised the fact that the structural details of a crystal must be taken into account; that the packing of spherical atoms is closer in some elements than in others; in other words, that the old meaning of atomic volume is of the nature of a fiction. It is therefore interesting to bring into the comparison the values of the true absolute volumes (for which the writer is responsible),

[15] Ann. Reports, 1917, 14, 233.   [16] A. Sommerfeld, op. cit., 105.

and also their ratios. The various results are embodied in the following table.

Table of Volume Constants.

	Na.	Mg.	Al.	Si.
Hull's absolute distances $(2r)$	3·72	3·22	2·86	$2·35 \times 10^{-8}$ cm.
True absolute "spherical" volumes..	26·9	17·5	12·2	$6·79 \times 10^{-24}$ c.c.
True atomic-volume ratios	1·00 :	0·65 :	0·45 :	0·25
Sommerfeld's theoretical ratios	1·00 :	0·57 :	0·42 :	0·33
Sommerfeld's cited ratios...	1·00 :	0·57 :	0·41 :	0·51

It is seen that the true atomic-volume ratios are in general agreement with Sommerfeld's theoretical values, and do not exhibit the great discrepancy 0·51 with respect to silicon—an apparent but not a real anomaly, which is simply due to the relatively open packing of the silicon (or diamond) structure. The general agreement is no doubt due to the relative simplicity of the problem of atomic volumes in the particular case of chemically uncombined elements.*

Recent Structural Models.

In view of the novelty and high degree of importance attached to the X-ray method, an attempt has always been made in these Reports to give complete lists of those models which appear to be well established. This custom will be adhered to on the present occasion.

Some Cubic and Hexagonal Elements and Compounds.—There are some fifteen substances which can be disposed of in the form

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* A brief note on the more salient aspects of atomic volumes in compounds may not be out of place. It might seem at the outset that the conversion of W. L. Bragg's absolute "atomic diameters" into corresponding spherical volumes (whereby the fluctuations naturally become of the order $\pm$ 30 per cent.) might throw light on such a perplexing problem as the undoubted volume equality of ammonium and rubidium compounds—a problem to which neither atomic weights nor atomic numbers bring any solution. Now the radius of the ammonium radicle can scarcely be greater than the sum of the radius of nitrogen and the diameter of hydrogen. As the latter diameter is generally accepted by physicists to be 10^{-8} cm., the radius of the radicle comes out to be $1·65(\times 10^{-8}$ cm.), which is much lower than 2·25, the radius of the rubidium atom. The corresponding spherical volumes are, of course, much further away from the expected ratio 1 : 1, being by calculation in the proportion 1 : 2·5. The nearest interpretation of this discrepancy is that an initially spherical or (as some mathematical physicists prefer) cubical atom suffers a deformation on entering into chemical union ; but the obvious difficulties which stand in the way of any precise definition of the new shapes, added to the possibility that atoms may change their volume on combination owing to a rearrangement or an actual transfer of electrons, would seem to demand the discovery of new methods of experimentation before real progress can be made.

H* 2

of a table. With the exception of thorium and nickel (determined by 'H. Bohlin),[17] all the values given below are due to Hull,[18] who says, apropos cobalt: " A finely powdered sample produced by rapid electrolysis showed a mixture of cubic and hexagonal close-packing in nearly equal ratio. After annealing in hydrogen at 600°, this sample showed only the cubic form. Another sample, composed of filings from pure cast metal, showed slight traces of hexagonal packing, due presumably to straining. It is possible that the other close-packed metals will behave in a similar manner, but this question has not been studied." According to Hull, ductility in a metal is a result of a face-centred cubic arrangement.

Table of some Cubic and Hexagonal Structures.

	Arrangement of atoms.	Grating distance of cube planes.	Distance between atomic centres.
Cobalt (dimorphous)...	Face-centred cube (cubic close-packed).	$1 \cdot 785 \times 10^{-8}$ cm.	$2 \cdot 52 \times 10^{-8}$ cm.
Thorium	Do.	2·56	3·62
Nickel	Do.	1·765	2·50
Rhodium	Do.	1·91	2·70
Platinum	Do.	2·01	2·85
Chromium	Centred cube	1·455	2·52
Molybdenum	Do.	1·575	2·73
Magnesium	Hexagonal close-packed.	—	3·22
Zinc	Do.	—	2·84
Cadmium	Do.	—	3·15
Cobalt (dimorphous)...	Do. •	—	2·53
Lithium fluoride*	Simple cube	2·01	2·01
Sodium fluoride*	Do.	2·31	2·31
Potassium fluoride* ...	Do.	2·69	2·69
Magnesium oxide* ...	Do.	2·11	2·11

* In these four cases the arrangement of like atoms is, of course, given by the face-centred cube.

Antimony.[19]—The nature of this structure is perhaps best grasped as follows. Suppose the familiar rock-salt cell, of Fig. 2, be set up with a solid diagonal vertical and then extended along it until the original cubic 90°-angle has attained the value 92° 53'. The edge of the cell must now be taken to be $3 \cdot 10 \times 10^{-8}$ cm.; the corresponding length of the vertical diagonal is 5·64. Now let the centres of the chlorine atoms be shifted through a vertical distance of 0·42 (exaggerated in Fig. 3), and finally suppose all the atoms to be replaced by antimony; the result is the antimony structure, which is the first example among elements of a "hexahedral" structure, that

[17] *Ann. Physik*, 1920, [iv], **61**, 421 ; *A.*, ii, 214.
[18] A. W. Hull, *Proc. Amer. Inst. Electrical Engineers*, 1919, **38**, 227.
[19] R. W. James and N. Tunstall, *Phil. Mag.*, 1920, [vi], **40**, 233 ; *A..* ii, 548.

is, one in which each atom is closely environed by six other atoms. In all previous cases of elementary substances the environment has always been tetrahedral, octahedral, or dodecahedral.

Zincite,[20] ZnO.—The crystal structure of this well-known dihexagonal polar mineral provides one of the few cases in which a verbal description is better than a diagram. Isomorphous with greenockite, CdS, and wurtzite, ZnS, it exhibits an interesting structural contrast to the commoner form of zinc sulphide—zinc blende. In both minerals the zinc atoms are essentially arranged in accordance with the principle of close-packing, the difference being that in zinc blende the " cubic " style of close packing is affected, in zincite the " hexagonal " style. In both structures the zinc (or cadmium) atoms are environed tetrahedrally by the sulphur (or oxygen) atoms.

FIG. 2.   FIG. 3.

○ = Na , ● = Cl .   ○ = Sb
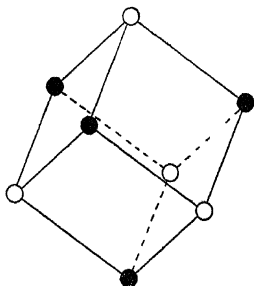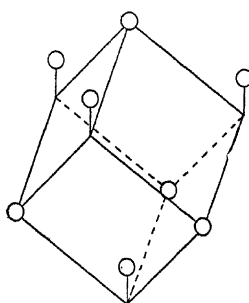
The absolute vertical distance in zincite between successive layers of similar atoms is 2·60, whilst the horizontal interval between adjacent atomic centres is 3·22. It is of interest to recall the fact that E. S. Fedorov[21] showed that two different structures are reconcilable with the preliminary observations recorded in W. H. and W. L. Braggs' well-known book, one of them demanding atomic polarity, the other being the structure finally adopted by W. L. Bragg.

The Calcite Group.—An *X*-ray study that has some bearing on the question of the existence of groups of atoms in crystals we owe to R. W. G. Wyckoff,[22] who has subjected calcite, rhodochrosite, chalybite, and magnesite (as also sodium nitrate[23]) to an investiga-

[20] W. L. Bragg, *Phil. Mag.*, 1920, [vi], **39**, 647 ; *A.*, ii, 433.

[21] *Bull. Acad. Sci. Petrograd*, 1916, **10**, 377.

[22] *Amer. J. Sci.*, 1920, [iv], **50**, 317.

[23] *Idem., Physical Rev.*, 1920, [ii], **16**, 149 ; *A.*, ii, 756.

tion by the Nishikawa method—essentially an ingenious combination of the Laue and de Broglie methods. The nature of some of these compounds has been previously elucidated by W. H. and W. L. Bragg, who explained their results in terms of a face-centred lattice, but the structures are, perhaps, best visualised as being the sodium chloride structure, which has been deformed along a three-fold axis until the cleavage cube has acquired the angles of the cleavage rhombohedron, the sodium and chlorine atoms being then regarded as substituted by calcium atoms and carbonate groups respectively. An inspection of Fig. 4 (which is drawn true to scale) will show that triads of oxygen atoms are relatively close to individual carbon centres. The main result of the new investigation is to show that these triads are at a constant distance of 1·22 Ångström units from their corresponding carbon atoms, although all other atomic distances vary considerably in passing from one car-

FIG. 4.   FIG. 5.
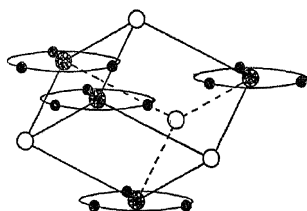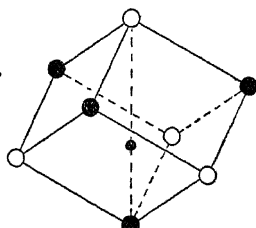
O = Ca, ⊕ = C, ● = O.   O = Cs, ⊕ = I, ● = Cl.

bonate to another—the distances between adjacent carbon and metallic atoms, for example, being 3·04 and 2·83 Å.U. in calcium and manganese carbonates respectively. This can be interpreted as evidence of the persistence in the crystal structure of the CO_3-groups, the internal details of which are, so to speak, no concern of the externally placed metallic ion.

Caesium Dichloroiodide, $CsCl_2I$.—The elucidation of this rhombohedral substance has been successfully accomplished by the same author [24] by means of the Nishikawa method. The lattice can be regarded as derived from the rock-salt type of structure, by a compression along a three-fold axis, until the cubic 90° angle has acquired the rhombohedral 80° 12′ value. The absolute dimension of this vertical length is $6·06 \times 10^{-8}$ cm.; caesium and iodine atoms are placed alternately at the corners. A chlorine atom is located

[24] R. W. G. Wyckoff, *J. Amer. Chem. Soc.*, 1920, **42**, 1100 ; *A.*, ii, 489.

on the principal axis of this cell at a distance equal to 0·62 times the cell-diagonal, from either the cæsium or the iodine atom.* The origin of this ambiguity lies in a circumstance peculiar to the chemical composition; the reflecting powers of the horizontal strata of cæsium and iodine atoms are approximately equal (on account of the close atomic weights or numbers of the elements concerned), and the strata are accordingly indistinguishable from each other by means of *X*-rays. . . . The writer therefore thought it would be interesting to examine the two questions: (1) whether the structure as determined by Wyckoff is reconcilable with W. L. Bragg's values of atomic diameters, and (2) whether the application of these atomic diameters serves to remove the ambiguity concerning the position of the chlorine atoms. The answers to both these questions would seem to be emphatic affirmatives. Figs. 6—7 represent
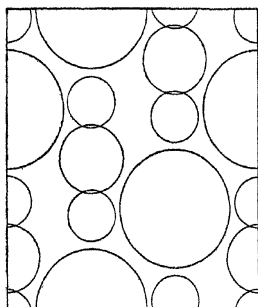
FIG. 6.   FIG. 7.
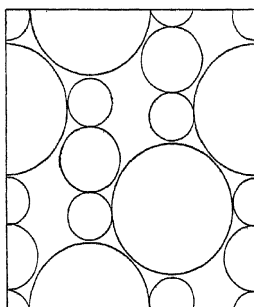
vertical elevations on the plane ($\bar{1}$10). In Fig. 6 W. L. Bragg's mean values, Cs=4·74; I=2·80; Cl=2·10, have been adopted; although there is a slight interpenetration of the iodine and chlorine spheres of influence, the spacial accommodation for the various spheres can be regarded as satisfactory. This interpenetration can be avoided and the general fit improved, without tampering with Wyckoff's data, if some such amended values as Cs=5·36, I=2·70, and Cl=1·90 be adopted (compare Fig. 7). In both figures the chlorine-centres have been taken as lying nearer to iodine than to cæsium; if the chlorine-centres lay nearer to cæsium, they would fall inside the cæsium atoms.

* Since each of the corner-atoms of the cell is really common to eight cells in an infinitely extended structure, and since the chlorine atom belongs wholly to the cell illustrated, it follows that the total cell-composition is $\frac{1}{8}(Cs_8I_4)Cl$, which is equivalent to $CsICl_2$.

Physical Crystallography.

This important branch of physics is poorer by the loss of Professor W. Voigt, of Göttingen, so celebrated for his experimental researches in elasticity and the many other abstruse properties of crystals requiring a highly mathematical treatment.

Electrolytic Conduction.—The many experimental difficulties which have long stood in the way of an exact study of electrolytic conduction in crystals have been recently overcome by Tubandt,[25] who has thereby opened up a new field of investigation (the abstract must be consulted for an account of the general method of experimentation). Since the specific conductivities of the compounds examined are very low at ordinary temperatures, the experiments were carried out in a stream of an indifferent gas at as high a temperature as practicable. This immediately led to the interesting observation that the specific conductivity of the cubic form of silver iodide (stable above 144·6°) is 3000 times as great as in the case of the hexagonal modification (both measured near the transition temperature), and if the measurement be effected close to the melting point the value is actually much higher for the solid than for the fused substance. Crystals of silver chloride, bromide, and iodide were found to behave as unidirectional electrolytes, permitting freely the migration of silver ions (in amounts which rigorously obey Faraday's law), but preventing all movement of halogen ions in the reverse direction. Lead chloride, however, behaves in exactly the opposite way, the negative chlorine ions migrating freely. The author points out that these trustworthy results of careful experiment are difficult to reconcile with a view that the crystal ions of binary compounds are held in equilibrium by electrostatic forces. The investigation of silver sulphide, of which there are two forms, $\beta \rightleftharpoons (179°)\alpha$, revealed a new point of interest. The high temperature α-modification behaves just like the halogen salts of silver, but with the β-form there is simultaneously an electronic conduction in the opposite direction, so that the crystal exhibits both electrolytic and metallic conduction. The author is disposed to refer this to the presence in the β-form of two kinds of molecules.

Ultramicroscopic Inclusions in Crystals.—It will be remembered that inorganic ultra-microscopic "colloidal" particles have been definitely proved to be crystalline by the use of the Debye-Scherrer-Hull method of X-ray exploration.[26] The investigation of minute

[25] C. Tubandt, *Mitt. Naturforsch. Ges. Halle,* 1917, **4**, 21 ; C. Tubandt and S. Eggert, *Zeitsch. anorg. Chem.,* 1920, **110**, 196 ; *A.,* ii, 279 ; C. Tubandt, *Zeitsch. Elektrochem.,* 1920, **26**, 360.   [26] *Ann. Reports,* 1919, **16**, 197.

particles in crystals by the help of the ultramicroscope is now proceeding. The beginnings of this work apparently lie in a suite of papers [27] on the nature of metal-fogs in crystals. It has been found that absolutely pure crystals of lead chloride, silver chloride, and bromide (that is, crystals of the ordinary substances which have been recently treated with halogen to transform any trace of free metal into haloid) are ultramicroscopically transparent. If this material is melted and treated with a trace of free metal or of a reducing agent like potassium cyanide, a metallic fog is produced in the re-solidified material. Novel results are obtained in the case of lead chloride, for owing to the strong double refraction of the crystal each speck of light, arising from an ultramicroscopic particle, is doubled and plane-polarised. Thallium chloride and bromide could not be obtained clear, since they cannot be treated with halogen without the formation of higher haloids.

The method has been more recently applied [28] to a study of the origin of opalescence in mixed crystals of sodium and potassium chloride, occasionally erupted by Vesuvius. The previous investigation of the binary system, NaCl–KCl by Nacken [29] was, of course, invaluable. The opalescence is due to a separation of the two components consequent on the temperature falling below the point of complete miscibility for a given mixture. It was instructive to observe the process in laboratory products of various compositions, as it gradually unfolded itself under the ultramicroscope. The crystal becomes doubly refracting, due to strains; then the separated particles reveal their existence, and finally strains and the double refraction disappear. The author proposes to attack the system orthoclase–albite, in which a primary homogeneous mixed crystal (" anorthoclase ") will no doubt eventually yield a micro- or cryptoperthitic structure.

Specific Heats of Minerals.—A monumental research on the specific heats of the various modifications of silica and of the more important silicates has been published by White,[30] who within the last few years has greatly improved the general technique of high temperature measurement. The constants directly determined were " interval-specific heats," that is, average specific heats over such ranges of temperature as 0—100°, 0—300°, 0—500°, and so on. From these values the specific heat at any desired temperature was deduced by two new methods, which gave perfectly consistent

[27] R. Lorenz and W. Eitel, *Zeitsch. anorg. Chem.*, 1915, **91**, 46, 57, 61; *A.*, 1915, ii, 260.

[28] W. Eitel, *Centr. Min.*, 1919, 173.

[29] R. Nacken, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 192; *A.*, 1919, ii, 281.

[30] W. P. White, *Amer. J. Sci.*, 1919, [iv], **47**, 1; *A.*, 1919, ii, 133.

results, and this when multiplied by the factor M/n (where M is the molecular weight, and n the number of atoms in the molecule), finally yields the mean atomic heat. At the ordinary temperature the value of the last-mentioned constant is of the order 3·3 for silica and 3·75 for silicates; it increases with rise of temperature, at first quite rapidly and then more gradually as it approaches a limiting value in the neighbourhood of 6·0. The results will no doubt have great significance in the future study of certain geological processes, but it may be noted that they have already an important bearing on various questions of great theoretical interest. The atomic heat at constant volume, for example, can be computed from the observed atomic heat at constant pressure by the help of a well-known thermodynamic formula, involving compressibility, thermal expansion, and density, but the computed value for cristobalite (according to Fenner [31] the stable modification of silica above 1470°) cannot be reconciled with generally accepted theoretical ideas, which must accordingly rest on a faulty basis. Moreover, the results obtained from a study of the various modifications of silica can be used as a test of the reasonableness of Smits' theory of dynamic allotropy,[32] and as a result of his painstaking work of precision the conclusion is drawn by White that it is possible to over-estimate the value of that theory.

Optics.—Attention must be called to a paper [33] on the general optical properties of amyrolin, $C_{14}H_{12}O_3$. This monoclinic substance exhibits an abnormally high birefringence (apparently only exceeded by calomel), and is also very noteworthy on account of a strong dispersion of the conical refraction. Two papers by A. Ehringhaus [34] on the dispersion of the birefringence of many substances are also worthy of a careful perusal.

Comparative Chemical Crystallography.

The progressive nature of the effects produced by a mutual substitution of the elements potassium, rubidium, and cæsium, as well as the close similarity of rubidium and ammonium compounds, which has been largely emphasised by Tutton's investigations during the last thirty years, is now so well known that it is only necessary to place on record a recent paper by this indefatigable worker [35] dealing with the compounds typified by the formula

[31] C. N. Fenner, *Trans. Soc. Glass Technology*, 1919, 3, 116.

[32] *Ann. Reports*, 1914, 11, 258.

[33] H. Rose, *Jahrb. Min.*, 1918, 1; *A.*, 1918, i, 266.

[34] *Ibid., Beil.-Bd.*, 1916, 41, 342; 1920, 43, 557.

[35] A. E. H. Tutton, *Proc. Roy. Soc.*, 1920, [A], 98, 67; *A.*, ii, 690.

$R_2Cu(SeO_4)_2.6H_2O$. There are also two papers to be noted refer‐ ring to series of organic compounds. The first, by A. Ries,[36] deals with an extensive series of mono‐, di‐, tri‐ and tetra‐alkyl deriv‐ atives of ammonium picrate, some of which have been previously examined by Jerusalem. The main results of this work are two in number: first, the prevalence of polymorphism in organic com‐ pounds (many of the substances appearing in three or four forms), and secondly, the regularity with which one of the modifications of every tetra‐substituted picrate is either strictly hexagonal or pseudo‐hexagonal. The theoretical interpretation of this regu‐ larity would have been easy if the substances concerned had been tri‐substituted. The second paper [37] deals with the series of com‐ pounds, typified by the general formula $R_4N\cdot HgI_3$, in which R represents various alkyl, aryl, or alphyl groups. One result is to prove that the racemic compound, dl‐$Ph(CH_2Ph)MeEtNHgI_3$, is isomorphous with the corresponding diethyl compound, which necessarily consists of identical and symmetrical molecules. Perhaps the most noteworthy features of the paper, however, are the omis‐ sion of all computed angles, as being unnecessary to any future purpose, and also the description of the methods devised in recent years, which serve to reduce the routine work of crystal description to about one‐third of that formerly required.

Methods of Investigating Opaque Substances.

Although opaque minerals are not relatively very numerous, they represent a highly important class of compounds, if only because of their supreme economic value. In the past the identification of opaque compounds has had to depend on such simple physical tests as density, cleavage, hardness, and streak (supported by the methods of chemical analysis), since the ordinary optical methods are only applicable to transparent substances; but in recent years more and more attention has been paid to those special microscopic methods introduced by Sorby, which have been developed more and more in connexion with metallography. This technique has been applied to minerals (notably in America). The new method has been recently expounded in at least two books,[38, 39] and a general account, together with a most valuable bibliography, has also been

[36] *Zeitsch. Kryst. Min.*, 1920, **55**, 454; *A.*, i, 715.

[37] T. V. Barker and (Miss) M. W. Porter, *T.*, 1920, **117**, 1303.

[38] J. Murdoch, "Microscopical Determination of the Opaque Minerals," 1916.

[39] W. M. Davy and C. M. Farnham, "Microscopic Examination of Ore Minerals," 1920.

ιgiven by a German worker.[40] The method has been variously named "Mineralography," "Opakography," and "Mineragraphy"—terms which are perhaps less pronounceable than "Chalcography" (suggested by Brauns).

The method consists essentially of the examination, under a microscope fitted for side-illumination, of the upper surface of a specimen which has been ground, polished, and possibly etched with various reagents. Both ordinary and plane polarised light are employed. In the latter case any opaque mineral that does not belong to the cubic system may reflect two plane or elliptically polarised rays, one of which is somewhat retarded (not, in general, to the same extent as in the case of transparent substances). The principles underlying the various optical effects have been recently treated very thoroughly by Wright,[41] who has also done much to perfect the finer technique.[42] The method has obviously a great future, not least on the purely scientific side, for it promises to lead to a revision of many opaque mineral species. It should also prove useful in the examination of dyes and lakes.

Thermal Studies of Mineral Systems.

Thermal studies of mineral systems are becoming so numerous that they cannot all be described with a fullness proportionate to their deserts. In making a selection, the writer is compelled to restrict himself to some relatively simple investigations, and, inferentially, to omit any consideration of the complex ternary system,[43] $CaO-MgO-SiO_2$, as also of Niggli's work [44] on certain mixed fusions involving the oxides of sodium, potassium, calcium, aluminium, carbon, silicon, and titanium. It is believed that the relatively simple cases will give a general idea of the significance of the present-day type of work, which is presumably the main object of this Report.

Binary Systems involving Barytes, Celestine, and Anhydrite.— In continuation of his previous work,[45] in which it was proved that barytes, celestine, and anhydrite pass into other modifications (probably monoclinic) at high temperatures, Grahmann [46] has investigated the miscibility relations of the substances over a vast

[40] H. Schneiderhöhn, *Jahrb. Min. Beil.-Bd.*, 1920, 43, 400.

[41] F. E. Wright, *Proc. Amer. Phil. Soc.*, 1919, 58, 401.

[42] *Idem, Mining and Metallurgy*, 1920. No. 158.

[43] J. B. Ferguson and H. E. Merwin, *Amer. J. Sci.*, 1919, [iv], 48, 81, 165; *A.*, 1919, ii, 401, 459.

[44] P. Niggli, *Zeitsch. anorg. Chem.*, 1916, 98, 241; *A.*, 1917, ii, 211.

[45] *Ann. Reports*, 1913, 10, 256.

[46] W. Grahmann, *Jahrb. Min.*, 1920, i, 1.

range of temperatures. The method adopted was that of cooling curves, supplemented by density determinations and by a study of the optical properties in thin sections. It is found that each pair of the α(high temperature)-modifications yields an uninterrupted series of mixed crystals. This is also true for the β(low temperature)-modifications of barium and strontium sulphates—in other words, for barytes and celestine. On the other hand, the miscibility of the β-modifications of calcium and strontium sulphates (anhydrite and celestine) is limited even at the high temperature of 1000°, and becomes more restricted at the ordinary temperature. Anhydrite can take up 42 mol. per cent. of strontium sulphate, and celestine up to 12 per cent. of calcium sulphate—the mixtures being isodimorphous in Retgers' sense. Anhydrite and barytes present a similar behaviour, but the miscibility is much more restricted, each being able to take up about 6 per cent. only of the other. The research is, of course, of considerable mineralogical interest, for it reveals miscibility possibilities far in excess of those actually observed in nature, as determined by mineral analyses.

Binary System Åkermanite–Gehlenite.[47]—The investigation of mixtures of these two compounds may be regarded as an excellent example of the experimental method of studying a perplexing mineral problem. Two distinct species—gehlenite,

$$3CaO, Al_2O_3, 2SiO_2,$$
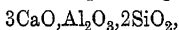
and melilite, $Na_2O, 11(Ca, Mg)O, 2(Al, Fe)_2O_3, 9SiO_2$—are usually recognised as belonging to the tetragonal "melilite group." With these must be reckoned the closely related åkermanite, an important constituent of furnace slags, which, according to Vogt, is essentially a calcium silicate, $4CaO, 3SiO_2$. Now a well-defined compound, $2CaO, MgO, 2SiO_2$, was found by Ferguson and Merwin to play an important rôle in the ternary system, $CaO–MgO–SiO_2$, and they concluded it to be åkermanite in its purest form; moreover, since a compound, $2CaO, Al_2O_3, SiO_2$, deemed to be pure gehlenite, had been previously prepared by Rankin and Wright, the investigation of the equilibrium relationships of gehlenite and åkermanite suggested itself as a method of attacking the difficult problem of the melilite group. It is found that the two isomorphous components form an uninterrupted series of mixed crystals exhibiting a minimum melting point (Roozeboom's type III). As gehlenite and åkermanite are respectively negative and positive optically, one of the mixtures (55 per cent. of åkermanite) is isotropic. (As a matter of fact, this inversion of optical character was observed by Vogt in the case of certain furnace slags, which he regarded as

[47] J. B. Ferguson and A. F. Buddington, *Amer. J. Sci.*, 1920, [iv], 50, 131; *A.*, ii, 621.

mixtures of gehlenite and åkermanite.) Another interesting item is that åkermanite glass has a higher density and refractive index than the crystalline modification. The authors hope to continue their work, so auspiciously begun, and there can be little doubt that the correct interpretation of the melilite group will not be long delayed.

Ternary System,[48] MgO–Al$_2$O$_3$–SiO$_2$.—The investigation of this system was beset with much difficulty owing to the high temperatures involved, which were frequently beyond the limits of the platinum furnace. The various binary compounds have been elucidated in previous researches and noted in these Reports. The only ternary compound is apparently a simplified cordierite,

$$2MgO,2Al_2O_3,5SiO_2,$$
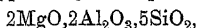
a phase which decomposes at a temperature lower than its melting point, but which can crystallise out of a complex mixture at somewhat lower temperatures. The compound is best prepared by holding a glass of like composition at temperatures lying between 900° and 1400°; an unstable form begins to appear at 900°, which goes over at a somewhat higher temperature to the stable form. The equilibrium relationships of this cordierite are somewhat complicated by the fact that it forms solid solutions with spinel, MgAl$_2$O$_4$, and sillimanite, Al$_2$SiO$_5$. Natural cordierite contains water, and part of the magnesia is replaced by ferrous oxide, but the general similarity in optical properties is sufficiently close to establish its identity with the synthetic, iron-free cordierite.

The Dehydration Process in Crystals ("Efflorescence").

The results of a comprehensive investigation of this process have been recently published by Gaudefroy.[49] Although not generally susceptible to ocular proof under the microscope, loss of water is almost certainly accompanied by a temporary local liquefaction. By way of a general support to this conclusion, Gaudefroy states that almost any finely powdered hydrate can be transformed into a coherent cake by simply allowing it to remain in a desiccator for a few hours. This behaviour he attributes to a temporary solution of the solid in the water which it is about to lose by evaporation. In at least one case a periodic liquefaction and solidification is directly observable under the microscope. Under certain conditions a crystal of the heptahydrated zinc sulphate becomes covered with monoclinic crystals of the hexahydrated salt, which extend their

[48] G. A. Rankin and H. E. Merwin, *Amer. J. Sci.*, 1918, [iv], **45**, 301 ; *A.*, 1918, ii, 199.

[49] C. Gaudefroy, *Bull. Soc. franç. Min.*, 1919, **42**, 284.

boundaries in a rhythmic manner. At various stages a tiny crystal of the hexahydrate is surrounded by a zone of liquefaction, into which it grows as water is eliminated. The loss of one molecule of water of crystallisation is accompanied by a contraction equal to about one-tenth of the original molecular volume; and the surface of the new crystal consists of a concentric system of furrows and ridges as a result of this periodic shrinkage.

Another general point of interest is that the inception of dehydration and consequently the local formation of a dehydration figure can be readily brought about by inoculation with a fragment either of the actual product of dehydration or of a substance isomorphous with it. Thus if an orthorhombic crystal of magnesium chromate, $MgCrO_4,7H_2O$, be simply touched by a crystal of the anorthic copper sulphate, $CuSO_4,5H_2O$, dehydration of the chromate to the pentahydrate begins immediately, and proceeds at such a rate as to be visible to the naked eye.

Many hydrated substances lose water of crystallisation in more than one well-defined stage. To each stage there corresponds a characteristic dehydration figure. Thus, ferrous sulphate, $FeSO_4,7H_2O$, either loses three molecules of water or one; in the former case the figures are elliptical, whilst in the latter case the boundaries are rectilinear, being, in fact, either triangles or trapezia. With many substances two or more kinds of transformation take place simultaneously, so that it becomes impossible by means of a chemical analysis to correlate each type of dehydration figure with the specific amount of water lost There are, however, other ways of deducing the composition of the different products. Thus the heptahydrated cobalt sulphate, unlike its isomorph ferrous sulphate, does not give the elliptical type of dehydration figure, but only the rectilinear type, and as the product can be proved by chemical analysis to be the hexahydrate, the same must be reasonably true of the corresponding type of figure given by ferrous sulphate. A confirmatory test is to drop small fragments of the dehydrated salt into a saturated solution of another salt; if the fragments grow isomorphously, their composition is thereby satisfactorily determined. This test is particularly trustworthy in the case of the vitriols, which have been so thoroughly investigated by previous workers from almost every conceivable point of view.

Following is a brief summary of the various types of dehydration figure revealed by Gaudefroy's researches.

Rectilinear Figures Determined by the Crystals under Dehydration.—Figures of this class are quite numerous, being, in fact, given in 54 per cent. of the substances examined. The dehydration takes place most favourably along certain selected planes of the

structural lattice, with the result that the dehydration figures on any given face are bounded by traces on that face of other important structural planes. By a study of the forms of the dehydration figure on the best developed faces of a crystal the " dehydration-polyhedron " can be determined, from which the dehydration figure for any other face can be deduced in the usual way. In the case of the monoclinic heptahydrated sulphates of iron and cobalt, the dehydration polyhedron is bounded by the forms $\{001\}$, $\{110\}$, and $\{10\bar{1}\}$. The material within the boundaries of a given dehydration figure is at first limpid, but soon becomes opaque; during the limpid stage it can be proved optically to consist of an irregular arrangement of minute crystals.

Rectilinear Figures Determined by the Product of Dehydration. —Each of these figures, in their simplest form, represents a single crystal of the new hydrate. The figures on any given face have accordingly no precise orientation. A good example is the hexahydrated decomposition product of ordinary zinc sulphate, which has already been mentioned as growing rhythmically.

Figures Exhibiting a Division into Four Sectors.—These are especially common in gypsum, the anorthic and orthorhombic vitriols, and the ferrocyanides. Opposite sectors are optically similar. The diagonals of the sectors are generally more distinct than the external boundaries, and have a definite orientation on each crystal face. The fine structure of the sectors is sometimes very complicated, but as a rule each sector is made up of a parallel bunch of fibres.

Elliptical Figures.—These figures are characterised by an extraordinarily fine texture of component particles arranged with every possible orientation. The figures are generally very deep-seated, and the internal surfaces are also curved. Wherever several kinds of dehydration figure are given by the same substance, the elliptical figures are characteristic of that chemical change which involves the greatest loss of water, and the excessively minute size of the component particles is attributed to the powerful disruptive effects of the correspondingly great contraction of molecular volume. It is interesting to note that the ratios of the ellipsoidal axes may differ widely in isomorphous substances. In zinc vitriol, for example, the ratios are $1 \cdot 1 : 1 : 1 \cdot 4$, whilst in the corresponding magnesium salt the ellipsoid practically becomes a sphere, and the figures on all the faces are substantially circles and not ellipses. In a monoclinic crystal one of the three ellipsoidal axes is always coincident with the symmetry axis, and in a uniaxial crystal the ellipsoid is one of rotation.

<div style="text-align: right">T. V. BARKER.</div>

RADIOACTIVITY.*

Nuclear Constitution of Atoms.

THE nuclear theory of the atom is based on the form of the trajectory of the α-particle in passing through the atom, which in turn is deduced from the deviation suffered by the α-particle in its passage.[1] The fact that the overwhelming majority of the α-particles pursue practically rectilinear trajectories, whilst a few of them are deviated more or less abruptly, led to the well-known conception of the atom as a system of sparsely distributed single electrons occupying the atomic volume, equal in number to the atomic number of the atom, with a concentrated countervailing positive charge, equal in magnitude to the combined charge of the electrons, at the centre of the atom, and constituting a nucleus of dimensions excessively small relatively to the atomic volume. The inference that this nucleus contains all but some 0·05 to 0·02 per cent. of the mass and weight of the atom follows from the known mass of the contained negative electrons, and is in general accord with the electrical theory of mass. According to this, the mass of an electric charge is proportional to the square of the charge and inversely proportional to its diameter. To account for its mass on this view, the diameter of the nucleus of the uranium atom would be 4×10^{-15} cm., or 1/50th of the diameter of the single negative electron, if it consisted of pure positive electricity. That the nucleus is not a pure positive charge, but contains negative electrons, the net charge being positive and equal to the atomic number, is shown by the emission of β-rays from the radio-elements and by the mode of formation of isotopes in radioactive changes. Hence the view is not free from inconsistencies.

Impact of α-Particles on Heavy Atoms.—Great improvements have been made in the comparison of the experimental results of scattering with the mathematical theory. The magnitude of the

[1] *Ann. Reports*, 1913, **10**, 271 ; compare also R. Seeliger, *Jahrb. Radioaktiv. Elektronik*, 1919, **16**, 19 ; *A.*, ii, 145.

nuclear charge for platinum, silver, and copper has been evaluated accurately by a determination of the ratio of α-particles scattered over a solid angle between 22° and 36·5°. This ratio is proportional to the square of the atomic number and a quantity depending on the velocity and known physical and instrumental constants. The minuteness of the ratio makes a direct determination, by comparing the number of α-particles scattered with those in the original beam, difficult. The difficulty was ingeniously overcome, however, by introducing a notched rotating disk into the path of the α-particles, when counting the direct beam, and so reducing them in a known ratio at will to a number comparable with the number scattered. In this case one obtains intermittent gusts of scintillations with any desired interval between, conditions which are very favourable to counting, and actually enable the number per second capable of being counted accurately to be five times as great as without the device. This is apart from the complete control over this number by varying the relative size of the notch.

The experimental values for the three metals named, 77·4, 46·3, 29·3, are, in each case, within the known probable error of the accepted values of the atomic numbers, 78, 47, and 29. This, incidentally, is an important confirmation of the correctness of the absolute magnitude of the atomic numbers, and shows that the Periodic Table contains no unsuspected vacant places.

With the same arrangements, it was possible to verify accurately the inverse-square law of force over the region in which scattering of the α-particle occurs for the platinum atom. The number of particles scattered, other conditions being constant, depends on the initial velocity of the α-particle raised to the power $4/(1-p)$, when the force around the nucleus deviating the particle varies as $1/r^p$, r being the distance. The experimental value of p found was between 1·97 and 2·03, a variation from the inverse-square law within the counting error of 4 per cent. The actual least distance of approach to the nucleus was between 7 and 14($\times 10^{-12}$ cm.) for high and low velocity α-particles respectively. From other experiments in this field and in that of the wave-lengths of the K-series of X-ray spectra, it follows that the inverse-square law holds over a range between 3 and 100($\times 10^{-12}$ cm.), and that there can be no electrons in this region in the case of a heavy atom like platinum. These are fundamental conclusions.[2]

Impact of α-Particles on Light Atoms.—Turning now to impacts of α-particles with the nuclei of light atoms, where the nucleus struck is violently repelled,[3] and itself constitutes a new type of

[2] J. Chadwick, *Phil. Mag.*, 1920, [vi], **40**, 734.

[3] *Ann. Reports*, 1914, **11**, 274 ; 1916, **13**, 261.

radiant particle, such as the H-particle resulting from the passage of α-rays through hydrogen, most striking results have been achieved. Here the α-particle approaches within $0.25(\times 10^{-12}$ cm.) of the hydrogen nucleus, and the results point to rapid changes and possibly to variations of the direction of the field of force within the distance 0.35. The inverse-square law no longer holds. Only one in 10^9 of the hydrogen atoms penetrated by the α-particle is repelled with a velocity sufficient to enable it to be detected beyond the range of the α-rays, or one H-particle is produced by a hundred thousand α-particles passing through 1 cm. of hydrogen gas at N.T.P. This number, though minute, is from ten to thirty times that to be expected if the inverse-square law held. The absorption of these H-particles over their range, which is four times that of the α-particle producing them, is reminiscent of the absorption of α-particles themselves, and is totally different from what is theoretically to be expected. With H-particles generated by long-range α-particles, over a range equivalent to 22 cm. of air, there is practically no diminution of the number of H-particles, whilst between this and the end of the range, 28 cm., there occurs a gradually increasing diminution. With H-particles generated by short-range α-particles, the theoretical curve is more nearly approached. The H-particles in the first case appear to be projected in the same direction as that in which the α-particle is travelling, or within a few degrees of it, all at the same velocity. It is clear that to this case, where a very intimate approach of the helium and hydrogen nuclei occurs, special considerations apply.[4]

The identity of these H-particles with hydrogen was proved by a determination of the deviation suffered in electromagnetic and electrostatic fields. The value of e/m found, 10^4, is in perfect accord with that of the hydrogen ion, 9570 (E.M.U.). Its velocity, namely, 1.6 times that of the α-particle generating it, is in perfect agreement with the maximum value calculated for a "head-on" collision. The charge is positive in sign, and no negatively charged particles were observed.[5]

With regard to light gases other than hydrogen, helium gives no particles differing in range from the generating α-particle. From this it is inferred that singly charged atoms of helium, the estimated range of which would be four times that of the α-particle, are not formed. But oxygen, nitrogen, air, and carbon dioxide all gave scintillations of similar brightness over a range of 2 cm. of

[4] (Sir) E. Rutherford, *Phil. Mag.*, 1919, [vi], **37**, 537; *A.*, 1919, ii, 256 L. B. Loeb, *ibid.*, **38**, 533; *A.*, ii, 145.

[5] (Sir) E. Rutherford, *ibid.*, 562; *A.*, 1919, ii, 258.

air beyond that of the range of the generating α-particles. The number was of the same order as those obtained in hydrogen gas. The range, 9 cm. of air, was only one-third as great, and the brightness of the scintillations, at a distance equivalent to 7·5 cm. of air, was equal to that of an α-particle at 1 cm. from the end of its range, instead of at 0·5 cm., as for the H-particle. The original presumption,[6] that these short-range particles were due to atoms of oxygen and nitrogen carrying unit charge, has now been shown to be at fault.[7] It has been found possible to determine their nature by special arrangements for the examination of their deflexion in a magnetic field, allowing the use of wide slits. Instead of the particles from oxygen being less deflected than the generating α-particles, as should be the case if they were singly charged atoms of oxygen, they were more deflected, which excludes the possibility that they can be oxygen atoms, either singly or doubly charged. A mass intermediate between 1 and 4 and a double charge were indicated. The deviation suffered was estimated to be 5 per cent. less than that suffered by H-particles in a direct comparison, and the conclusion was drawn that they consist of doubly charged positive particles of mass about 3 with a velocity 1·2 times that of the generating α-particle. There was no noticeable difference between oxygen and nitrogen, so far as these short-range particles are concerned. Both appear to yield a new particle of mass 3, differing from the "H_3" of positive-ray methods of gas analysis in that it carries two units instead of one of positive electricity, and therefore is presumably an isotope of helium.

Nitrogen, however, differed sharply from oxygen in giving, in addition to these new particles, a very much smaller number (about one-twelfth) of H-particles. The range of these is slightly greater than of those obtained from hydrogen, but their identity was proved by direct comparison of the electromagnetic deviation in the apparatus above referred to.[8] It is estimated that, to produce 1 cubic millimetre of hydrogen by this means, the total α-radiation of 2 kilograms of radium acting for a year would be required.

So far as can be seen, artificial disintegrations of atoms by collision with the α-particle appear to be endothermic. The particle of mass 3 appears to escape with rather more than the energy of the α-particle striking the nucleus of the oxygen or nitrogen atom. Even neglecting the kinetic energy of the residue of the nucleus and of the α-particle after the collision, the dis-

[6] (Sir) E. Rutherford, *Phil. Mag.*, 1919, [vi], **37**, 571 ; *A.*, 1919, ii, 259.

[7] *Ibid.*, Bakerian Lecture, *Proc. Roy. Soc.*, 1920, [A], **97**, 374 ; *A.*, ii, 541.

[8] *Ibid., loc. cit.*, and *Phil. Mag.*, 1919, [vi], **37**, 581; *A.*, 1919, ii, 260.

integration, as in the case of the radio-elements themselves, must be accompaṅied by the liberation of energy. On the view that the actual energy required to bring about the disintegration is small, and that the energy of the α-particle is mainly expended against the strong repulsive field, in getting near enough to the nucleus to affect it, electrons or β-rays, which would move up to the nucleus in an attracting field, may be able to bring about similar changes. This raises anew the whole question, so frequently discussed in these Reports,[9] as to the origin of the helium, found by some and not by other investigators, after passage of the electric discharge through gases in vacuum tubes and in old X-ray bulbs and the like. The latest experimental contribution gave negative results, in so far as the discharge through carefully purified hydrogen is concerned. In no case was helium or neon detected.[10] Naturally, these highly significant results have produced a flood of speculation as to the constitution of the atomic nucleus, which does not yet call for consideration here.

Isotopes.

Our knowledge of the heterogeneity of common elements has been notably advanced, during the period under review, beyond that recorded in the Reports four and seven years ago,[11] by the perfection of the positive-ray method of gas analysis and its application to the detection of heterogeneity, if it exists, in some nineteen non-radioactive elements.[12] The methods depend on the same general principles as those which sufficed to detect the presence of meta-neon, of atomic mass 22, in atmospheric neon in 1913, but the electromagnetic and electrostatic deviating fields are rearranged in such a way as to secure an effect precisely analogous to focussing in optics. The trajectories of the positive ions in a slightly divergent beam are brought to a focus in a plane containing the photographic plate. All those for which the value of the mass divided by the charge is the same are brought to the same point in the plane, those with greater and less values, respectively, being on either side. The complex pencil is resolved into a "mass spectrum" in every respect analogous to a light spectrum produced by a prism or grating. The terms "first-order and second-

[9] *Ann. Reports*, 1914, **11**, 45, 289.

[10] A. Piutti and E. Cardoso, *Gazzetta*, 1920, **50**, i, 5; *A.*, ii, 311.

[11] *Ann. Reports*, 1916, **13**, 245; 1913, **10**, 265.

[12] F. W. Aston, *Nature*, 1919, **104**, 334, 393; 1920, **105**, 8, 547; **106**, 468; *Phil. Mag.*, 1919, [vi], **39**, 449, 611; **40**, 628; *A.*, ii, 277, 344, 718.

order mass-spectrum" are used to denote spectra produced by ions singly and doubly charged respectively. The existence of ions with more than one unit of charge introduces a complication, but fortunately these are experimental peculiarities which enable the two orders usually to be distinguished without uncertainty. The relative mass of the ion causing any line in the spectrum can so be evaluated to an accuracy of one part in a thousand, and the atomic mass determined to a degree of accuracy comparable with that attained in the best determinations of the atomic weight by chemical means. Incidentally, the complete agreement between the two in many cases affords much the most important evidence of the constancy between mass and weight for different elements. This question has been much canvassed of recent years.

Of the nineteen elements so far examined, ten prove to be homogeneous and nine to be heterogeneous and composed of more than one isotope with different atomic masses. The following table, taken from the author's last communication to *Nature*, gives the results.

TABLE OF ELEMENTS AND ISOTOPES.

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Masses of isotopes, in order of their intensity.
Hydrogen	1	1·008	1	1·008
Helium	2	3·99	1	4
Boron	5	10·90	2	11, 10
Carbon	6	12·00	1	12
Nitrogen	7	14·01	1	14
Oxygen	8	16·00	1	16
Fluorine	9	19·00	1	19
Neon	10	20·20	2	20, 22, (21)
Silicon	14	28·30	2	28, 29, (30)
Phosphorus	15	31·04	1	31
Sulphur	16	32·06	1	32
Chlorine	17	35·46	2	35, 37, (39)
Argon	18	39·88	2	40, 36
Arsenic	33	74·96	1	75
Bromine	35	79·92	2	79, 81
Krypton	36	82·92	6	84, 86, 82, 83, 80, 78
Iodine	53	126·92	1	127
Xenon	54	130·32	5 (7)	129, 132, 131, 134, 136, (128, 130 ?)
Mercury	80	200·60	(6)	(197–200), 202, 204

(Numbers in brackets are provisional only.)

Apart from a possible uncertainty, already alluded to, as to the order of spectrum to which any line belongs, the photographs published reveal the great power and certainty of the new method. Unfortunately, only non-metallic elements have so far been included. The difficulties in the way of examining metallic elements by this means have not yet been overcome.

In every case, except hydrogen, the atomic mass of each homogeneous component proves to be an exact integer, in terms of that of oxygen as 16, within the error of measurement already stated. For hydrogen, however, the chemical value, 1·008, is exactly confirmed and its homogeneity proved. Hydrogen, of course, is an exception to every generalisation concerning the chemical elements, and its simple structure, consisting probably of a single positive charge as nucleus and a single electron as satellite, is a sufficient reason for its uniqueness. If the hydrogen nucleus is the elementary positive constituent of the nuclei of other atoms, a number of electrons, equal to the difference between the atomic weight and atomic number, must be present also. Thus, if the nucleus of uranium is made up of 238 hydrogen nuclei, there must be in the nucleus $238-92=146$ electrons. The close packing of these positive and negative constituents may account for the difference of mass, 1·9 units, between the mass of the constituents and that of the resulting atom, that is, essentially to the difference in the atomic weights on the basis $H=1$ and $O=16$.[18]

The integral value of the atomic weights then points to an atomic constitution of secondary units, such as helium nuclei, packed sufficiently openly not to influence their mutual masses, the whole of the packing effect being due to the close packing within these secondary units.

Isotopes of Lead.

Atomic Weight of Lead of Radioactive Origin.—Fuller details of the atomic weight determination of the lead from Norwegian thorite, which gave 207·9, the highest yet found, have been published, together with those found for lead from three Ceylon thorianites, particulars of which follow: [14]

	Per cent. Th.	Per cent. U.	Per cent. Pb.	At. wt.
I.	68·9	11·8	2·3	207·21
II.	62·7	20·2	3·1	206·90
III.	57·0	26·8	3·5	206·83

Lead separated from samarskite, containing 12·2 per cent. of U_3O_8 and 1·03 per cent. of ThO_2, gave the value 206·30.[15] Lead from a Japanese source, of possible, though doubtful, radioactive origin, gave the value 207·13, which does not differ appreciably from that of common lead.[16]

[13] Compare *Ann. Reports*, 1916, **13**, 253.

[14] Compare *Ann. Reports*, 1918, **15**, 201; O. Hönigschmid, *Zeitsch. Elektrochem.*, 1919, **25**, 91; *A.*, 1919, ii, 285.

[15] A. L. Davis, *J. Physical Chem.*, 1918, **22**, 631; *A.*, 1919, ii, 107.

[16] T. W. Richards and J. Sameshima, *J. Amer. Chem. Soc.*, 1920, **42**, 928; *A.*, ii, 434.

Melting Point.—Two determinations show that, within the error of measurement, the melting point of lead of radioactive origin is identical with that of common lead. In one,[17] the lead, compared with common lead, had the atomic weight 206·57. A constantin-manganin couple was used, and the melting points were found to be identical to 0·5°, the experimental error. In the other,[18] thermocouples of copper–nickel were employed, the single couple being capable of reading hundredths, and the multiple couple thousandths, of a degree.

The lead compared in this case was from an Australian radio-active mineral of atomic weight 206·6. Neither specimen was spectroscopically pure, the common lead being the less pure, but probably the impurities did not exceed 0·005 per cent. They showed slight differences of behaviour. The super-cooling was greater for the purer sample, and its freezing-point–time curve was more horizontal. The radioactive lead had the higher melting point by 0·05°, but part, if not all, of this difference is to be ascribed to its greater purity. The thermo-electric power, electric conductivity, and change of the latter with temperature and pressure, were for each sample the same. These negative results thus have now decided between opposing theoretical views before discussed.[19]

Spectrum.—The minute difference, 0·0043 Å., in the wave-length of the line 4058 Å., already reported, has been confirmed.[20] Ordinary lead, lead from Joachimsthal pitchblende of undeter-mined atomic weight, and lead from Ceylon thorite of atomic weight 207·77, were compared. The method consisted in photographing the respective interference fringes, produced by a Fabry and Perot *étalon*, the source of light being an arc between an alloy of cadmium with the lead and a button of tungsten in a vacuum. Important sources of error present in the first series of experi-ments,[21] which gave a negative result, were eliminated by reducing all observations to a selected cadmium fringe as standard, which registers any variation due to a change of temperature or to the wandering of the source of light. These causes affect the standard fringe equally with the fringe under examination, and are so eliminated. The wave-length for the pitchblende lead was found to be 0·0050 Å.±0·0007 Å. greater than that for ordinary lead,

[17] M. Lembert. *Zeitsch. Elektrochem.*, 1920, **26**, 59; *A.*, ii, 216.

[18] T. W. Richards and N. F. Hall, *J. Amer. Chem. Soc.*, 1920, **42**, 1550; *A.*, ii, 622.

[19] *Ann. Reports*, 1916, **13**, 252.

[20] Compare *Ann. Reports*, 1918, **15**, 204; T. R. Merton, *Proc. Roy. Soc.*, 1920, [A], **96**, 388; *A.*, ii, 140.   [21] *Ann. Reports*, 1916, **13**, 248.

which, in turn, was 0 0022 Å.±0·0008 Å. greater than that for thorite lead. Also, a difference was found for the wave-length of the line 5350 Å. of thallium when ordinary thallium and the thallium contained in pitchblende residues were compared, the former being the greater by 0·0055 Å.±0·001 Å. In this case, owing to the thallium not having been separated from the residues, the result cannot be entirely depended on, for the displacement of lines, by the presence of impurities, in the arc spectrum, though rare, is not entirely unknown. But it indicates a presumption that the thallium in pitchblende is of radioactive origin and different in atomic weight from ordinary thallium.

In an interesting discussion of the spectra of isotopes,[22] it is pointed out that the differences in the case of lead, although only of the order of a millionth of the wave-length, are one hundred times greater than are to be expected from the Bohr theory, as corrected to take into account the displacement of the centre of mass of the vibrating system with a change of the mass of the nucleus. They are enormously greater than can be ascribed to any purely gravitational effect of the mass of the nucleus on the electron. The result indicates the existence of a force, due to the mass of the nucleus, on the electronic system of the atom not hitherto known. In the original experiments, in which a 25 cm. grating was used and the spectrum photographed in the sixth order, the line was shifted, not broadened, to a position corresponding with the mean atomic weight of the lead, although a broadening, if not an actual resolution, into two or more lines corresponding with the separate isotopes present, in these circumstances, although not in the subsequent *étalon* experiments, is apparently to be expected. This minute difference of wave-length of the lines in the spectrum is the only difference in the physico-chemical properties of isotopes, apart from atomic mass, so far substantiated.

Separation and Properties of Isotopes.

It cannot yet be considered proved beyond doubt that any actual analytical separation of the components of a mixture of isotopes has been effected. Systematic fractionation of atmospheric neon by the use of cold charcoal failed to effect any separation.. Even fractional diffusion through pipe-clay has not, so far, given consistently positive results.[23] The theoretical question of the possi-

[22] W. D. Harkins and L. Aronberg, *J. Amer. Chem. Soc.*, 1920, **42**, 1328 ; *A.*, ii, 541.

[23] F. A. Lindemann and F. W. Aston, *Phil. Mag.*, 1919, [vi], **37**, 523 ; *A.*, 1919, ii, 209.

bility of separation by various means has been much discussed.[24] Methods, such as fractional diffusion, centrifugal separation, and thermal diffusion, which depend on differences of molecular mass, if not those, such as vaporisation and chemical fractionation, ought theoretically to be effective. The thermal diffusion method, depending on the maintenance of two intercommunicating vessels at widely different temperatures, which produces a condition of equilibrium, in which excess of the heavier constituent is present in the colder vessel, and centrifuging. both appear promising from the theoretical point of view.

Preliminary announcements of the partial separation of the isotopes of chlorine, mercury, and iodine (!) have been made. In the first case,[25] indications of a separation of hydrogen chloride by fractional diffusion into a heavier and lighter fraction have been announced, but no definite experimental data are given. In the case of mercury,[26] evaporation at low pressure is stated to give a condensate less in density than the residual mercury. Each fraction was redistilled before the density was taken, and the difference in the pyknometer determinations amounted to 5 parts in 100,000, the error of measurement being less than one part in a million. Iodine, the most recent of the elements to be submitted to positive ray analysis, and found, unlike chlorine and bromine, to be homogeneous, has, from speculative reasoning, been ascribed five isotopes. Fractional diffusion gave products with atomic weight varying from 128·22 upward, the mean being 2·04 per cent. above the accepted value.[27]

Very interesting new results have been obtained along the lines of the use of radioactive isotopes of common metals to indicate what is occurring to the latter in chemical operations. Thus it has been shown that a free exchange of the metallic atom among the competing acid radicles occurs for ionised, but not for non-ionised, compounds. The general method was to mix solutions of two different compounds of lead in equimolecular proportions, the one compound only being "activated" by presence of thorium-B, which is isotopic with lead, and to determine the activity of the lead in the less soluble compound crystallising out. When active lead nitrate and inactive lead chloride are dissolved in molecular

[24] F. A. Lindemann, *Phil. Mag.*, 1919, [vi], **38**, 173; S. Chapman, *ibid.*, 182; *A.*, 1919, ii, 390.

[25] W. D. Harkins, *Nature*, 1920, **105**, 230; *Science*, 1920, **51**, 289.

[26] J. N. Brönsted and G. von Hevesy, *Nature*, 1920, **106**, 144.

[27] E. Kohlweiler, *Zeitsch. physikal. Chem.*, 1920, **94**, 513; **95**, 95; *A.*, ii, 610, 615.

proportion in boiling pyridine, the lead in the lead chloride crystallising out is half as active as the lead in the original lead nitrate, but when an active lead salt is so mixed with an organic compound of lead, such as lead tetraphenyl or diphenyl nitrate, in suitable solvents, no interchange of lead occurs, and the active lead salt retains its original activity. This constitutes something like a direct proof of the ionic dissociation theory and of the current views as to the difference between the nature of chemical union in electrolytes and non-electrolytes. When the acetates of quadrivalent activated lead and of bivalent inactive lead are mixed in glacial acetic acid, the activity of the first compound, after crystallising out from the mixture, is reduced to one-half. This indicates, since the two lead ions differ only by two electrons, a free interchange of electrons between them and a dynamic equilibrium between ions and electrons, and between free electrons and the electrodes in electrolysis.[28]

Isotopes have been used to determine the velocity of diffusion of molecules among themselves. The rate of diffusion is dependent on the molecular diameter, and not on the mass, so that a radioactive isotope diffusing among the inactive molecules of the same type of element affords the means for investigating experimentally this otherwise insoluble problem. The case has been tried with molten lead. At the bottom of a narrow, vertical tube was placed a layer of lead rendered active by the presence of thorium-B, and above it a layer three times the height of common lead. The whole was kept at 340° for several days. After cooling, the cylinder was cut up into four equal lengths, each melted and hammered into foil, and the concentration of thorium-B in each determined by α-ray measurements. Values for the diffusion coefficient between 1·77 and 2·54 per sq. cm. per day, with a mean of 2·22 in seventeen experiments, were obtained. This corresponds with a diameter of the lead molecule between 0·78 and 1·16($\times 10^{-8}$ cm.), according to the formulæ used to connect the two quantities. The value found, when reduced to a temperature of 18° and for a fluid of the viscosity of water, becomes 2·13. Since the value for lead ions diffusing in aqueous solutions is 0·68, this indicates that the molecular diameter in the case of metallic lead is only a third of that in the case of the ion, and shows that the latter is probably hydrated.[29]

[28] G. von Hevesy and L. Zechmeister, *Ber.*, 1920, **53**, [B], 410 ; *A.*, ii, 278 ; *Zeitsch. Elektrochem.*, 1920, **26**, 151 ; *A.*, ii, 345.
[29] J. Gróh and G. von Hevesy, *Ann. Physik*, 1920, [iv], **63**, 85 ; *A.*, ii, 739.

Researches analogous to those reported have led to the detection and isolation of volatile hydrides of lead and tin.[30]

The "Fixed Electron" Type of Atomic Structure.

A notable rival has been developed to the view described in the last Report [31] of an atom in which the electrons are supposed to revolve in orbits around the nucleus, with special assumptions as regards the radiation of energy in quanta rather than continuously. In this atom, the electrons surrounding the nucleus are supposed to occupy, or oscillate about, certain fixed positions in the structure. This fixed electron type of atom has been found to possess many advantages in chemistry and physics, notably in accounting for the Periodic Law, the various categories of chemical compounds, ionised and un-ionised, and the arrangement of the atoms in the crystal space-lattice as determined by X-ray methods. It may be said to draw its underlying postulates from facts in these fields rather than from any purely mathematical or fundamental reasoning.[32] The chief idea is that, in the outermost shell of electrons surrounding the nucleus, the electrons tend to form an octet and to occupy the corners of a cube. In the outermost shell all eight corners are occupied in those atomic structures corresponding with the zero family of chemically inert gases. The chemical activity of other elements is due to some of the corners being not occupied by electrons, whereby two or more atoms tend chemically to "combine." The combination may be of two kinds. Either the atoms with only a few of the corners occupied by electrons, that is, of those elements in the first families of the Periodic Table, lose their electrons altogether, forming positive ions, such as $Na^{.}$, $Mg^{..}$, $Al^{...}$, to the atoms which have all but a few of the corners occupied, that is, of those elements in the last families of the Periodic Table, with the formation of the negative ions, such as Cl', S'', or more often to groups of these atoms. This way of regarding ionised compounds was, of course, arrived at long before this theory was proposed, but it emphasises the completely separated existence of the two ions forming the molecule, even in the solid state, which is supported by the character of the space lattices of the crystals

[30] Ann. Reports, 1918, 15, 225; 1916, 13, 266; F. Paneth and K. Fürth, Ber., 1919, 52, [B], 2020; F. Paneth and O. Nörring, ibid., 1920, 53, [B], 1693; A., ii, 41, 758.

[31] Ann. Reports, 1918, 15, 206.

[32] G. N. Lewis, J. Amer. Chem. Soc., 1916, 38, 762; A., 1916, ii, 310; I. Langmuir, Proc. Nat. Acad. Sci., 1919, 5, 252; J. Amer. Chem. Soc., 1919, 41, 868, 1543; 1920, 42, 274; A., 1919, ii, 328, 506; 1920, ii, 243; Science, 1920, 51, 605; A., ii, 656; W. Kossel, Zeitsch. Physik, 1920, 1, 395; A., ii, 681.

of salts. The forces at work are the opposed charges on the ions which act statistically, n sodium ions requiring the simultaneous presence of n chlorine ions, rather than each sodium atom being attached to one chlorine atom, as in the formula Na–Cl.

In the second kind of combination, namely, that corresponding with definite atomic linkings, such as are regarded to exist between the atoms of the molecule in organic compounds and in non-electrolytes generally, the theory is more original. Different atoms so rigidly linked together are regarded as sharing electrons in pairs. Two electrons held in common by two atoms constitute the ordinary single bond. The cubes are attached edge to edge. Four electrons in common correspond with a double bond. The cubes are attached face to face. A corner to corner attachment of two cubes, which the single bond most closely suggests, is not considered to occur at all. The sharing of a pair of electrons by two atoms is regarded as the single unit of valency.

In addition to this type of definite linkage, two others are postulated. The hydrogen nucleus is capable of sharing a pair of electrons, its own and one derived from another atom, either an atom of itself, as in the hydrogen molecule, or an atom containing an uncompleted octet. Thus in water the oxygen nucleus is at the centre of a cube of electrons, two pairs of which, at two opposite pairs of contiguous corners, being shared with two external hydrogen nuclei. Pairs so held are supposed to be drawn closer together, distorting the cube. In this way, the tetrahedral character of the carbon atom is accounted for. The uncombined atom of carbon, if it existed free, which, of course, never occurs, would have four of the eight corners of the cube occupied with electrons. If symmetrically distributed, these would occupy the corners of a regular tetrahedron. When it shares these in pairs with electrons of other radicles or atoms in compounds, the drawing together of each pair shared preserves the tetrahedral character of the arrangement in the combined atom. The facts of stereo-chemistry require free rotation to be possible about a single bond, and not about a double bond, whereas, unless further assumptions are made, such as that the pair are drawn together to one point or supposed to rotate round one another, free rotation would not be a possibility for a single linkage on this theory. The existence of triple bonds again, which is possible on a tetrahedral, is impossible on a cubic atom, if only partly deformed to a tetrahedron.

The second type of combination postulated is rather surprising in that a pair of nuclei are supposed to be contained in a single cube, or octet, in such combinations as the nitrogen molecule,

carbon monoxide, hydrocyanic acid, and nitric oxide. If this is correct, such compounds would represent, as it were, structures half-way between those typical of atoms and molecules respectively. Although something might be said for such a structure representing the properties of nitrogen, one would scarcely have expected it to be capable of representing also such an extremely active gas as nitric oxide.

Into this theory of valency, which so far seems to be confined mainly to the lighter elements in the earlier part of the Periodic Table, it is unnecessary further to enter here. Of more topical significance is the way in which the atomic numbers of the Periodic Law are accounted for. The atom is regarded as made up of concentric shells of electrons of relative diameter 1, 2, 3, 4, and relative area 1, 4, 9, 16. Each electron is regarded as occupying the same superficial area, to whatever shell it belongs. The inert gases are the elements for which the outer shell contains its full complement of electrons. Helium, of atomic number 2, has two electrons at the poles of the first shell. The line joining them and passing through the nucleus is regarded as the polar axis of the atom. The plane passing through the equator divides the shell into two hemispheres. There are no electrons in the equatorial plane of any atom. In the outer shells, concentric with the first, they are distributed according to the symmetry of a tetragonal crystal. Four secondary planes of symmetry, at 45° with each other, pass through the polar axis. The second completed shell, being four times the area of the first, contains eight electrons, occupying the eight corners of a cube. This is the neon atom. The atomic number is 10, and it contains eight electrons in the second shell—four in each hemisphere above and below the equatorial plane—and two in the first, or helium, shell. Every shell, other than the innermost, after getting filled up with electrons once, is filled up twice, and the next inert gas is argon, atomic number 18, containing sixteen electrons in its second shell and two electrons in its first. In the next, krypton, of atomic number 36, the third shell contains eighteen electrons, two distributed at the poles and the other sixteen symmetrically with regard to the polar axis and the sixteen underlying electrons of the second shell. By filling the third shell again we get xenon, of atomic number 54. The fourth shell contains thirty-two electrons, and the next inert gas must have an atomic number 86. This is the correct atomic number for the emanations of the radioactive elements. Unfortunately, the Periodic Table comes to an end before this ingenious theory can be further tested. That, however, the table should proceed to uranium, which possesses complete chemical analogy to tungsten

and molybdenum, instead of to a second lot of rare earth elements, after radium and thorium, raises the doubt whether it just does not come to an end in time for the theory. Undoubtedly, however, it is an achievement, even by such arbitrary assumptions, to have accounted for the actual sequence of elements in the table at all.

The theory has found general support in the explanation of the arrangements of atoms in crystals as elucidated by X-ray methods.[33] It is possible to assign to each atom in the space-lattice a definite approximate diameter, and to regard the crystal as built of spheres of these diameters closely packed. When the atomic volumes corresponding with these diameters are plotted against atomic weights, a curve, in every respect analogous to Lothar Meyer's atomic volume curve, is obtained, but applicable to the compounds of the elements. Then it is found that two electronegative elements are situated close together, and are assigned small diameters when, according to the above theory, they share electrons; but the electropositive elements, which exist as separated ions and do not share electrons with their neighbours, are situated at a distance from them, and appear to have large diameters. From crystal data, the diameter of the electronic shells corresponding with neon, argon, krypton, and xenon are put at 1·30, 2·05, 2·35, and 2·70 Ångström units respectively. The theory, being definite and easily visualised, if arbitrary, will doubtless justify itself in drawing attention to the many different types of chemical interaction, which hitherto have been too liable to be confused together and forced into a mould to fit just the one type of interaction which the ordinary valency-bond theory suffices to explain. It is not yet possible to bridge the gap between this idea and that of the rotating electron atom, which has grown up largely from the study of the wave-lengths of the characteristic X-rays themselves. Undoubtedly each type has its advantages, but for chemistry the fixed electron type seems easily to hold the field.

In the light of these advances, an experiment showing that the α-radiation from different faces of a large crystal of uranium nitrate was, within the error of experiment, of the same intensity, seems to show that the α-particles are shot out from the nucleus during disintegration, without relation to the orientation of the atomic axis, for it may be regarded as at least highly probable that in the crystal space-lattice the atoms have their axes orientated in a regular manner.[34]

[33] W. L. Bragg, Royal Institution Evening Lecture, May 28th, 1920; *Phil. Mag.*, 1920, [vi], **40**, 169; *A.*, ii, 537.
[34] T. R. Merton, *Phil. Mag.*, 1919, [vi], **28**, 463; *A.*, 1919, ii, 453.

High-frequency Spectra of the Elements.[35]

Work in this field proceeds apace, though without breaking much fresh ground. Precision measurements, to a degree of accuracy one-hundredfold greater than previously, have been carried out for the lines in the K series of a number of elements from chlorine to copper, and the results compared with the various mathematical formulæ proposed. The spectrum of tungsten, for which the K, L, and M series can all be studied, has also been examined, and a spectrograph constructed to bridge the gap between these two series of precision measurements.[36] The M series has been further investigated, and extended from uranium as far as dysprosium.[37]

New measurements of the absorption bands of thulium, neoytterbium, and lutecium in the K series have been made.[38]

An examination of the L absorption spectrum of a pure radium chloride solution gave two lines, 0·802 and 0·670 Å., in agreement with the atomic number 88 assigned by the Periodic Table.[39] By the use of a reinforcing screen of calcium tungstate, the β_1 line of the K spectrum of tungsten (0·1844 Å.) has been shown to be a doublet separated by about 0·0007 Å.[40] In an examination of the X-ray absorption spectrum of phosphorus, differences of wave-length were observed for different forms. The wave-length 5·767 Å. was found for the black phosphorus of Bridgeman, and 5·750 Å. for phosphoric acid and its ammonium salt, whilst red phosphorus shows a double limit, corresponding with each of the two wave-lengths given. This is believed to be the first case noticed of the chemical state of an element affecting its X-ray spectrum.[41]

Arrangements have been described for the examination of the space-lattices of powdered materials, by which it has been shown that thorium and nickel in powder form have face-centred cubical lattices, and magnesium a lattice composed of two interpenetrating simple hexagonal lattices.[42]

X-Rays have also been used to determine the size and structure of the particles of organic and inorganic colloids. Gold and silver

[35] Compare *Ann. Reports*, 1916, **13**, 257.

[36] M. Siegbahn, *Phil. Mag.*, 1919, [vi], **37**, 601 ; **38**, 639 (and with A. B. Leide), 647 ; *A.*, 1919, ii, 261, 488, 489 ; E. Hjalmar, *Zeitsch. Physik*, 1920, **1**, 439 ; *A.*, ii, 655.

[37] W. Stenström, *Ann. Physik*, 1918, [iv], **57**, 347 ; *A.*, 1919, ii, 90.

[38] M. de Broglie, *Compt. rend.*, 1920, **170**, 725 ; *A.*, ii, 277.

[39] *Ibid.*, 1919, **168**, 854 ; **169**, 134 ; *A.*, 1919, ii, 207, 358.

[40] *Ibid.*, 1920, **170**, 1053 ; *A.*, ii, 344.

[41] J. Bergengren, *ibid.*, 1920, **171**, 624 ; *A.*, ii, 654.

[42] H. Bohlin, *Ann. Physik*, 1920, [iv], **61**, 421 ; *A.*, ii, 214 ; compare A. W. Hull, *J. Amer. Chem. Soc.*, 1919, **41**, 1168 ; *A.*, 1919, ii, 470.

in the colloid form possess the same space-lattices as in large crystals, even when the particles are too small to be visible under the ultramicroscope. In old silicic acid and stannic acid gels, traces of crystalline structure can be detected, but not in the typical organic colloids, such as albumin, gelatin, cellulose, starch, and the like.[43]

It has been pointed out that it is a necessary consequence of the modern views of crystal structure that, in certain cases, the chemical composition of the crystal must depend on its size. Thus iron pyrites, with a space-lattice consisting of an atom of sulphur within a cube, four alternate corners of which are occupied by iron atoms, instead of the formula FeS_2 must possess a composition given by $Fe_{(n+1)^3}S_{2n^3}$, where n is the number of elementary cubes in the crystal. If n is 50, the particle would still be visible by the aid of the ultramicroscope, and its composition would be given by $FeS_{1.885}$.[44]

α-Rays.

The Geiger-Nuttall Relation.—The logarithmic connexion between the period of average life of an atom and the range of the α-ray expelled from it during disintegration, and the theory of the cause of atomic disintegration to which it has led, have been the subject of closer examination. On this theory,[45] the instability of the atom is supposed to result from the simultaneous conjunction of a large number, N, of separate particles, moving independently of one another within the atomic nucleus, in a certain favourable relation. The chance of disintegration depends on something like the one-hundred-and-sixtieth power of the velocity of the α-particle expelled, and such a law can scarcely be explained except as an expression of the probability of the fortuitous occurrence of a very large number of independent events.

The actual value first deduced from the periods and ranges for N was about 80, a number of the same order as the atomic number. The relation between range and period on this theory becomes

$$\log \lambda = Na + \tfrac{2}{3}N \log R,$$

where R is the range and a is, approximately at least, a constant.

From new data on the ranges of some of the members of the various disintegration series, values for N, 81, 77, and 71, have been assigned for the uranium–radium, thorium, and actinium series respectively.[46] Clearly these must be of the nature of mean

[43] P. Scherrer, *Nachr. Ges. Wiss. Göttingen*, 1918, 96; *A.*, 1919, ii, 274.

[44] A. Quartaroli, *Gazzetta*, 1920, **50**, ii, 60; *A.*, ii, 609.

[45] *Ann. Reports*, 1916, **13**, 257.

[46] S. Meyer, V. F. Hess, and F. Paneth, *Sitzungsber. Akad. Wiss. Wien*, 1914, **123**, 2a, 1459; S. Meyer, *ibid.*, 1916, **125**, 2a, 201.

values, since the number of independently moving particles in the nucleus must diminish by unity with each α- or β-particle expelled, that is, with each step in the disintegration series. The experimental numbers given for the uranium–radium and the thorium series agree with the mean values to be expected if the atomic nuclei are practically composed of helium nuclei and binding electrons. Thus for thorium, with atomic weight 232 and atomic number 90, 58 helium nuclei and $116 - 90 = 26$ binding electrons would constitute a system consisting of eighty-four independent units. The value of N for thorium itself would be one less, since the probability relation holds between one of the particles and the rest of the nucleus. The mean value for the series between thorium and thorium-C, considering N to be reduced by unity for each α- and for each β-particle expelled, would be 78 instead of the value found, 77. For the uranium atom, with atomic weight 238 and atomic number 92, two hydrogen nuclei at least must be postulated. If there are only two, there must be 59 helium nuclei and $118 + 2 - 92 = 28$ binding electrons, making a total of 89 independent particles. The mean of the number, diminished by one, is, for the series uranium to polonium, 81 or 82, again in excellent agreement with the experimental value.

If, now, the correct values for N are introduced for each member of the series, and the value of the constant a calculated, it is found that a is truly constant for the middle members of each series, but is markedly, although not greatly, different for the first and last members of each series.[47] The actinium series is scarcely yet worth consideration here, as, in absence of all experimental evidence as to the atomic weights of its members, the values to be assigned to N must be a matter for speculation. In addition, it obeys the logarithmic relation only very imperfectly. The difficult question as to the cause of the disintegration of the atom in radioactive changes seems at least to be progressing towards a satisfactory and highly suggestive answer.

In other papers, Bohr's principle of angular momentum has been applied to the internal economy of the nucleus, and the conclusion reached that the motions of the particles remaining in the nucleus are not affected by the successive steps in the atomic disintegration. The radius of the orbit of revolution of the α-particle in the nucleus before expulsion has been calculated, and found to diminish by steps with each successive disintegration.[48]

A collection of papers has appeared on the counting and photo-

[47] G. Kirsch, *Physikal. Zeitsch.*, 1920, **21**, 452 ; *A.*, ii, 577.
[48] H. T. Wolff, *ibid.*, 175, 393 ; *A.*, ii, 366, 578.

graphic registration of α-particles. The electrometer method, using high potential gradients just below the sparking potential, whereby the ionisation is enormously magnified by collision, has been the one employed. As the most suitable gas for filling the counting chamber, a mixture of 54 per cent. of carbon dioxide and 46 per cent. of air was used. It was found that a mixture of carbon dioxide and air, with the former in excess, responded only to the α-rays, and not to the β- and γ-rays.

A new determination of the number of α-particles expelled per second per gram of radium (element), free from disintegration products, gave $3.72(\pm 0.02) \times 10^{10}$. In arriving at this value, 80,000 α-particles were counted. This is about 4 per cent. above the previously accepted value, even after correction in terms of the International Standard.[49]

In a special research, it was found that 1·5 milligrams per sq. cm. of mica, of density 2·87, correspond, in stopping power towards α-rays, with 1 cm. of air at 760 mm. and 15°.[50]

The individual intervals between the emission of α-particles by polonium have been systematically studied by photographic registration methods for the case of 10,000 emissions. The requirement of the theory of probability was very exactly verified. The fraction of the total number of intervals of duration greater than τ is $\epsilon^{-\theta/\tau}$, where θ is the mean interval. For very short intervals the law is departed from, owing to the emission of α-particles with intervals between them too small to be distinguished by the means employed. From the results obtained, the number of such "doublets" could be very exactly evaluated.[51]

An effect, analogous to the "sputtering" of metals under the action of the cathode rays in discharge tubes, has been observed with α-rays for the noble metals nickel and aluminium, but not for such metals as copper, the surface of which is easily oxidised by the action of the atmosphere. Another effect due to α-rays was observed with polonium, electrolytically deposited on metal foil. The α-particles emitted at grazing incidence appear to "knock off" the polonium in aggregates of several molecules at a time, causing an effect analogous to the volatilisation of the polonium, which is called "aggregate recoil." The effect is very much more pronounced in a vacuum than in the atmosphere. It is greatest with freshly deposited preparations, and diminishes with their age.

[49] Ann. Reports, 1914, 11, 274.
[50] R. W. Lawson and V. F. Hess, Sitzungsber. Akad. Wiss. Wien, 1918, 127, 2a, 405, 461, 535, 599, 943.
[51] (Mme) M. Curie, J. Phys. Radium, 1920, [vi], 1, 12; A., ii, 727.

The most regular results are obtained with palladium and platinum foils electrolytically saturated with oxygen. Saturating with hydrogen diminishes the effects and makes them irregular.[52]

γ-Rays.

In a continuation of the researches fully described in the last Report,[52a] two types of secondary γ-rays, referred to as S_1 and S_2, have been found to be associated with the two primary components of the γ-rays of radium, designated as K_1 and K_2. The first is of the nature of a scattered primary, possessing the same coefficient of absorption as K_1, and distributed with decreasing intensity with increasing angle of scattering. None is detectable at an angle of 90° or beyond, or, in other words, this secondary radiation is confined to emergence. For this type, the scattering power of different atoms is proportional to their atomic number. The type S_2 is, in general, different in penetrating power from K_2, and is scattered over an angle of 180°, constituting an incident, as well as emergent, radiation. For light atoms the scattering is proportional to the atomic number, but for heavy atoms to the square of this number.[53] The absorption of divergent beams of γ-rays has also been studied, with the view of throwing light on the reason why γ-rays, although complex and scattered, so nearly obey the theoretical law of absorption to be expected for a homogeneous, non-scattered beam.[54]

Methods have been developed for " counting " γ-rays analogous to those referred to under " α-Rays." The effect of a γ- or β-ray is, in general, twenty to twenty-five times less than that of an α-ray, but with a sufficiently sensitive counting arrangement they may be counted with ease and certainty. Some special precautions are taken, on account of the high potential necessary to render the response very sensitive, but otherwise the arrangements are very much as for the α-rays. The gas used in the counting chamber is air, drawn from the free atmosphere and stored over sulphuric acid until any emanation initially present has had time to decay, and filled into the chamber through cotton wool and phosphoric oxide.

The γ-ray acts by liberating a high-velocity β-particle from the metal walls of the counting chamber, and the same methods are

[52] R. W. Lawson, *Sitzungsber. Akad. Wiss. Wien,* 1918, **127**, 2a, 1315; 1919, **128**, 2a, 795.

[52a] *Ann. Reports,* 1918, **15**, 211.

[53] K. W. F. Kohlrausch, *Sitzungsber. Akad. Wiss. Wien,* 1919, **128**, 2a, 853.

[54] *Ann. Reports,* 1918, **15**, 213 ; M. Blau, *Sitzungsber. Akad. Wiss. Wien,* 1918, **127**, 2a, 1253.

equally applicable for β- as for γ-rays. It was found that the number of γ-rays given per atom from radium-B and radium-C, respectively, were practically the same. The total number of γ-rays from both together is, in terms of the number of α-particles from radium-C, between two and one.[55]

Chemical Actions of the Rays of Radium.

The reactions proceeding in common gases, when mixed with radium emanation, and due to α-rays, have been the subject of two exhaustive investigations, chiefly to ascertain whether the facts are in agreement with the theory that the reactions obey a form of Faraday's law, that the molecules formed in the reaction are equal in number to the pairs of ions formed from the rays in the gas.[56] In one research, four gases, hydrogen sulphide, ammonia, nitrous oxide, and carbon dioxide, were studied. Other conditions being the same, the amount of decomposition is proportional to the amount of emanation present. The decomposition increases as the size of the reaction vessel is increased, to a limit corresponding with the state in which practically the whole of the energy of the α-rays is spent in traversing the gas molecules. For hydrogen sulphide, the thermal coefficient of the velocity of reaction is practically zero from $-180°$ to $18°$, and above this, to $220°$, is slightly negative. For nitrous oxide, the reaction proceeds probably in two directions, for the most part with the formation of nitrogen and oxygen, but also with the formation of nitric oxide and nitrogen. The accumulation of nitrogen peroxide as a result of the second reaction retards the reaction. Here, again, changes of temperature produce but a slight effect on the velocity of reaction, the coefficient being negative below and positive above $18°$. For ammonia, the coefficient is positive and considerable up to $220°$. Carbon dioxide was found to undergo only a very slight decomposition, and the rapid change recorded by other investigators is attributed to the effect of mercury and phosphorus in the vessel.

For these reactions, Faraday's law was found not to apply. The ratio between the number of molecules produced and the number of pairs of ions formed by the α-rays exceeds unity in cases where no catalytic action is involved.[57]

In the other research, the combination of hydrogen and oxygen was re-studied. Here it was found that 3·92 molecules of water result for every pair of ions formed in the gas. It appears that

[55] V. F. Hess and R. W. Lawson, *Sitzungsber. Akad. Wiss. Wien*, 1916, 125, 2a, 285, 585, 661.   [56] *Ann. Reports*, 1912, 9, 322.

[57] E. Wourtzel, *Le Radium*, 1919, 11, 289, 332; *A.*, ii, 214.

in all the earlier results of Ramsay and Cameron, which gave support to the ionisation theory, the amount of emanation used had been much overestimated. It had been calculated from the time of accumulation and quantity of radium, which, since the development of exact methods of measuring the emanation by the γ-rays, is known to be quite untrustworthy. The velocity of reaction was found to be proportional to the quantity of emanation and independent of the temperature. It was increased by increase of oxygen above the stoicheiometrical proportion, the velocity of reaction continuing to rise as this excess increases with the reaction, and diminished by increase of hydrogen, the velocity continuing to fall as the excess of hydrogen increases. This is to be expected from the ionisation theory, since the relative ionisations in oxygen and hydrogen are as 1·09 to 0·24, that of air being unity.

In very small vessels, particularly at low pressures, the velocity of reaction is abnormally high. This is ascribed to the atom of radium-A, recoiling from the atom of emanation, bringing about the combination in the same way as an α-particle. Under the most favourable conditions for magnifying this recoil effect relatively to that produced by the α-rays, it may exceed the latter six or seven times. The relative effect produced is in agreement with the data as to the magnitude of the ionisation produced by recoil atoms.

With the single exception of hydrogen and chlorine, where the chemical action may be several thousand times as great as the ionisation theory requires, it is claimed that there is a general statistical agreement between the number of ions and the number of molecules produced for a large number of reactions. The two numbers are not the same, but they correspond within a multiplier of a few units only in either direction. This is true for reactions produced by the cathode rays and β-rays, as well as those resulting from the action of α-rays and recoil atoms. The ratio of four to one, in the present case, between the numbers of the molecules and ions can be explained by ionic possibilities, without recourse to other theories.[58]

In the reverse reaction, the decomposition of liquid water by the α-particle into hydrogen and oxygen, about one molecule of water is decomposed per pair of ions formed. In practice, the recombination of hydrogen and oxygen under the action of the emanation proceeds almost to completion at constant volume, because the water condenses to droplets, and so is removed for the most part from the action of the α-rays.[59]

[58] S. C. Lind, *J. Amer. Chem. Soc.*, 1919, **41**, 531, 551 : *A.*, 1919, ii, 210.
[59] *Idem, Trans. Amer. Electrochem. Soc.*, 1918, **34**, 211.

The long series of parallel experiments on the action of the penetrating rays of radium and of ultra-violet radiation from a quartz mercury lamp on organic substances has been continued. The substances studied comprise a mixture of maleic and fumaric acids, solutions of formic and benzoic acids and of carbamide, dry and wet toluene, chloroform, and carbon tetrachloride. The effects of the two kinds of irradiation are, in general, similar, the ultra-violet light being usually almost incomparably the more rapid. The results bear out the general view that these agents have a shattering effect on almost all molecules, followed by numerous secondary reactions among the products.[60]

The thermoluminescence and decolorisation of glass which has been exposed to the rays of radium, on heating, have been shown to be independent of one another. For freshly exposed glass, thermoluminescence starts on heating below 100°, and at 200° for specimens exposed some years previously. Decolorisation does not, however, occur until the temperature of 500° is reached.[61] The colorations and thermoluminescence produced in a great variety of minerals have been examined. The fluorspars, by reason of the almost bewildering variety of colour changes they undergo and the brilliance of the thermoluminescence produced, are among the most interesting.[62] In this connexion, the variety of fluorspar from Wölsenberg, Bavaria, locally called "Stinkfluss," deserves special mention. On being crushed, it emits a peculiar odour, which those who have made a careful study of the mineral assert is without doubt due to free fluorine. Radium rays easily reproduce the natural dark blue colour in the mineral after the colour has been discharged by heating, but do not restore its odoriferous quality.[63]

Studies of Radioactive Minerals.

Age of Thorium Minerals.—In a careful review of the difficult questions connected with the age of thorium minerals, both the isotopes of lead derived from thorium are regarded as stable, and the age of the mineral, A, is deduced from the formula

$$A = \frac{Pb}{U + 0\cdot384\ Th} \times 7,900\ \text{million years,}$$

where Pb, U, and Th are the percentages of these elements in the

[60] A. Kailan, *Zeitsch. physikal. Chem.*, 1920, **95**, 215; *A.*, ii, 576; *Sitzungsber. Akad. Wiss. Wien*, 1919, **128**, 2a, 831; 1917, **126**, 2a, 741.

[61] S. C. Lind, *J. Physical Chem.*, 1920, **24**, 437; *A.*, ii, 576.

[62] E. Newbery and H. Lupton, *Mem. Manchester Phil. Soc.*, 1918, **62**, No. 10; *A.*, 1919, ii, 130.

[63] F. Henrich, *Zeitsch. angew. Chem.*, 1920, **33**, 5, 13, 20; *A.*, ii, 216.

mineral. The conclusion is reached that in (1) the Middle-Devonian formation at Brevig, Norway, in the Precambrian formations of (2) Arendal-Gegend, Norway, and (3) Moss, Norway, and (4) in the thorianite-bearing pegmatites of Ceylon, all those minerals with less than three times as much thorium as uranium give quite concordant ages for the formations, namely, (1) 300, (2) 1300, (3) 950, (4) 500 million years, respectively. These must be regarded as true primary minerals; but all those for which the Th/U ratio is greater than 3 give smaller ages, and must be regarded as secondary minerals derived from the primary by various processes of change in which the content of thorium has been enriched. In the first class are to be found, in (1) eudidymite, eucolite, zircon, pyrochlor, and biotite, in (2) clèveite, in (3) broeggerite, and in (4) pitchblende and thorianite, whilst in the second class are, in (1) freyalith, thorite, and orangeite, in (2) uranothorite and orangeite, in (3) uranothorite of Hitterö, and in (4) thorite. The atomic weights of the lead from the three varieties of thorianite, already given, conform well to the view that they are primary constituents of the pegmatite, which has an age between 400 and 500 million years.[64]

The ratio of thorium to uranium in a number of minerals has been determined by radioactive methods. In Morogoro pitchblende there is 0·5 per cent. of thorium and 74·5 per cent. of uranium; in pitchblende of St. Joachimsthal, per gram of uranium, $4·68 \times 10^{-5}$ grams of thorium, making, with the estimated $1·96 \times 10^{-5}$ grams of ionium, a total $6·64 \times 10^{-5}$ grams of thorium isotopes. A monazite sand of unstated origin, containing 7·23 per cent. of thorium, was found to contain 0·087 per cent. of uranium.[65] In another estimation, monazite sand from Brazil was found to contain 0·8, and from India 0·102 ($\times 10^{-9}$ gram of radium per gram). These correspond with 0·235 and 0·03 per cent. of uranium respectively, and, on a thorium content of 4 and 9 per cent., mesothorium preparations obtained from them would owe 28 and 2·1 per cent., respectively, of their initial γ-activity to radium.[66]

In a monograph on broggerite, which contained 63—66 per cent. of uranium, 6—6·5 per cent. of thorium, 9·5—10 per cent. of lead, and 0·7—1·5 per cent. of rare earths, hydrofluoric acid

[64] R. W. Lawson, *Sitzungsber. Akad. Wiss. Wien*, 1917, **126**, 2a, 721; *A.*, ii, 149.

[65] S. Meyer, *ibid.*, 1919, **128**, 2a, 897; *A.*, ii, 548.

[66] J. E. Underwood and H. Schlundt, *Trans. Amer. Electrochem. Soc.*, 1918, **34**, 203; *A.*, ii, 146. (In the abstract, 10^{-7} gram should read 10^{-9} gram.)

was found to be the best precipitant for thorium in presence of uranium. As is well known, the method of separation based on the solubility of uranium nitrate in ether or acetone is useless. The Pb/U ratio in this mineral is essentially constant at 0·12 to 0·13, which corresponds well with the age of about a thousand million years, already given, for the pegmatite dykes in the granites of Moss, Norway, from which it is obtained.[67]

The Uranium–Radium Ratio.—This important ratio has been redetermined for a carefully selected Colorado pitchblende. The uranium was estimated analytically, and the radium by the emanation method against specially made absolute standards of radium. These were prepared, by dilution to $1·5 \times 10^{-9}$ grams of radium per c.c., from a radium chloride of 100 per cent. purity, measured against the International Standard by γ-rays. A million times the quantity of barium was added to the diluted standard to protect the minute amount of radium from precipitation. The result gave $3·4 \times 10^{-7}$ grams of radium as the quantity in equilibrium with 1 gram of uranium. This was the original "Rutherford-Boltwood" value, but it was subsequently corrected to $3·23 \times 10^{-7}$ on the International Standard. Much independent work has shown that the uncorrected value was substantially correct, and it is very satisfactory to have had this conclusion confirmed so convincingly.[68]

Relative α-Activities of Uranium and Radium.—Many points remain to be cleared up with regard to the relative α-activities of radium and uranium minerals. A new determination has substantially confirmed the original determinations. Taking the activity contributed by uranium (U-*I* and U-*II*) as unity, the total activity of the mineral is now found to be 4·73 instead of 4·69, and the part due to radium itself as 0·488 in place of 0·45. If, however, the radium were produced from the uranium in a direct line without branching, its α-ray activity, calculated from the law that the ionisation is proportional to the two-thirds power of the range of the α-particles, should be 0·57. The value found, 0·488, can only be accounted for if the actinium branch claims either 26 per cent. of the atoms disintegrating if it starts from uranium-*I*, or 14 per cent. if it starts from uranium-*II*. From the proportion of the total activity contributed by the actinium

[67] E. Gleditsch, *Archiv for Mathematik og Naturvidenskab, Christiania,* 1919, **36**, Nr. 1; compare A. Fleck, *T.,* 1913, **103**, 384.
[68] S. C. Lind and L. D. Roberts, *J. Amer. Chem. Soc.,* 1920, **42**, 1170; *A.,* ii, 463; compare Becker and Jannasch, *Jahrb. Radioaktiv. Elektronik,* 1915, **12**, 1; F. Soddy and (Miss) A. F. R. Hitchens, *Phil. Mag.,* 1915, [vi], **30**, 218; *A.,* 1915, ii, 726; E. Gleditsch, *loc. cit.*

series, estimated from both the new and the old measurements as 0·26 to 0·28 in terms of that of the uraniums as unity, a branching factor of 8 per cent. for the actinium series has hitherto been accepted, but work about to be considered has reduced this to 3 per cent. or less, so that a real inconsistency between the experimental data and our theoretical interpretation exists, the clearing up of which might throw much light on the branching of the series.[69]

The Uranium–Actinium Ratio.—In a study of the pitchblendes of Morogoro and St. Joachimsthal, broeggerite from Norway, and two thorianites from Ceylon, representing extremes of Th/U ratio, the constancy of proportionality between radium, and therefore uranium, and actinium has been confirmed. Since the thorium-uranium ratio varied between the limits of 6×10^{-5} and 6, the independence of actinium and thorium, and the genetic connexion between actinium and uranium, follow.[70]

The Uranium-X–Uranium-Y Ratio.—For uranium derived from the same materials, the constancy of proportionality in the rates of production of uranium-X and -Y was established, and the genetic connexion extended to the supposed first member of the actinium branch series, uranium-Y. In this work, periods of average life for uranium-X_1 of 34·37 days, and for uranium-Y of 35·53 hours, were found. The former is slightly, and the latter considerably, less than the previously accepted values, namely, 35·5 days and 52·8 hours.

The method adopted for separating from uranium the uranium-X_1 and -Y, both being isotopes of thorium, consisted in neutralising the strong uranium solution with sodium hydroxide (not potassium hydroxide or ammonia) and adding a small quantity of a solution of a cerous salt and hydrofluoric acid. The cerous fluoride carries down with it the thorium isotopes, and is redissolved in hydrochloric acid. A milligram of dissolved zirconium is added, and the solution is precipitated with a solution of sodium hydrogen hypophosphate, $NaHPO_3,3H_2O$, according to the method of Koss. This precipitates the thorium isotopes with the zirconium and leaves the cerous salt dissolved. The relative activity of uranium-X_1 and -Y proved to be independent of the source of the uranium, and from it a branching factor for the actinium series of at most 4·2 per cent. was deduced.[71]

[69] *Ann. Reports,* 1909, **6,** 259; J. H. L. Johnstone and B. B. Boltwood, *Phil. Mag.,* 1920, [vi], **40,** 50; *A.,* ii, 523.

[70] S. Meyer and V. F. Hess, *Sitzungsber. Akad. Wiss. Wien,* 1919, **128,** 2a, 909; *A.,* ii, 658.

[71] G. Kirsch, *ibid.,* 1920, **129,** 2a, 309; compare M. Koss, *Chem. Zeit.,* 1912, **36,** 686; *A.,* 1912, ii, 809.

Parent of Actinium.—Details have been published of the separation of the direct parent of actinium, proto-actinium or ekatantalum, from pitchblende residues.[72] By prolonged and repeated treatment with nitric acid, the other radioactive constituents, including radium, may be almost completely removed. A little tantalum oxide is then added, and the material extracted with hydrofluoric and sulphuric acids. The addition of a few milligrams of thorium and lead nitrates at this stage serves to keep traces of ionium, uranium-X, and radio-lead in the insoluble form. The filtrate is evaporated to dryness, which leaves the tantalum and proto-actinium in an insoluble form, from which impurities, such as iron, zirconia, and the like, may be removed by boiling with aqua regia. So far, all attempts to separate proto-actinium from tantalum have failed.

By various elaborations of this method, the whole of the proto-actinium from pitchblende containing a known amount of uranium was carefully separated, and its α-activity measured. If the branching factor of the actinium series were 8 per cent., the preparation should have an α-activity equal to 4 per cent. of that of the uranium in the mineral. As a mean of six determinations, it was found that the branching factor was only 3 per cent. The completeness of the separation and the avoidance of loss during the chemical treatment were proved by carefully chosen tests with a previously prepared and measured preparation.

Period of Actinium.—From these proto-actinium preparations, a new and independent determination of the life of actinium was arrived at in the following manner. From the known ranges of the six α-rays of the actinium series, including that of proto-actinium, it follows that the initial α-activity of proto-actinium must be in the ratio $1:5\cdot74$ to the α-activity of the substance after equilibrium with the five α-ray-giving members of the actinium series has been attained. The proportionate increase of the α-activity over periods from 400 to 600 days corresponds with a half-period for actinium of 20 years, or to a period of average life of $28\cdot8$ years. This is in good agreement with the further results obtained by observations on the decay of activity of actinium itself, so that the period of actinium may now be regarded as known with reasonable certainty.[73]

[72] *Ann. Reports*, 1918, **15**, 195.

[73] O. Hahn and L. Meitner, *Ber.*, 1919, [B], **52**, 1812; *A.*, ii, 147, 148 ; *Physikal. Zeitsch.*, 1919, **20**, 529 ; *A.*, 1919, ii, 209.

Various.

Radioactivity of Rubidium.—An examination of the very feebly penetrating β-activity of rubidium compounds has confirmed the view that it is an atomic property of rubidium, and is unaffected by chemical purification or treatment. The rays are somewhat more penetrating than those of uranium-X_1,

$$[\mu_{Al} = 347 - 308(\text{cm.})^{-1},$$

as compared with 463 for the β-rays of uranium-X_1 and 312 for those of radium]. Their velocity is estimated as 0·6 that of light. The activity is feeble. A surface covered with 0·025 gram of rubidium sulphate per sq. cm. possesses the same activity as one covered with 0·00033 gram of uranium oxide per sq. cm. (total β-rays). Eliminating the penetrating β-rays of uranium-X_2, and extrapolating to a film of zero thickness, so correcting for absorption, it is estimated that the specific activity of the element rubidium is one-fifteenth of that of uranium, due to the change of uranium-X_1. The product of the change, if the normal law is followed, should be an isotope of strontium. It is suggested that the search for calcium, strontium, and cæsium, respectively, in minerals containing potassium, rubidium, and cæsium, and the determination of their atomic weight, if found, might throw further light on the radioactivity of the alkali metals.[74]

Changes in the Radioactivity of the Oxides of Uranium.—Some results in this field incompatible with the present theory of radioactivity have been recorded. The α-activity of various preparations of oxide of uranium showed a diminution over a term of years from 1 to 31 per cent. The greater decreases occurred with the green oxide, prepared by the gentle ignition of ammonium uranate, and the smaller with the black oxide, obtained by strong ignition of the nitrate, preparations of intermediate colour showing intermediate behaviour. In a preparation the α-activity of which had fallen from an initial value 5·95 to 4·64, the initial activity was restored by solution in nitric acid and ignition. It is unfortunate, perhaps, that no changes of weight of the preparations were looked for, for such results might be due to the possible, although hitherto unobserved, gain of oxygen or moisture by the feebly ignited green oxides from the atmosphere. On the other hand, from the impurities separated from the uranium, increases in α-activity from 7 to 93 per cent. were observed, the rate of increase in one case corresponding with a period of 1·1 months.[75]

[74] O. Hahn and M. Rothenbach, *Physikal. Zeitsch.*, 1919, **20**, 194; *A.*, 1919, ii, 312.   [75] C. Staehling, *Compt. rend.*, 1919, **169**, 1036; *A.*, ii, 5.

Period of Ionium.—The minute growth of radium from large amounts of carefully purified uranium, already recorded, has since proceeded regularly according to the square of the time, and a definite estimate of the period of ionium can now be deduced from the measurements. This is the same as that already provisionally calculated. Actually, the product of the periods of average life of ionium and radium alone is involved, and this, to an uncertainty of at most 5 per cent., is 237,500,000 years. The period of ionium is thus 100,000 years if that of radium is 2375 years. The actual growth of radium from 3 kilograms of uranium (element) in 10 years has been 2×10^{-10} gram.[76]

Fractional Crystallisation of Radium and Mesothorium from Barium.—The theory and practice of the enrichment of radium and mesothorium from barium in the fractional crystallisation of the chloride and bromide has been the subject of two communications. The enrichment factor, K, is defined as the ratio of the active material in the crystals to that in the original material in the solution. As regards the chloride, K varies from 1·65 for an acidity 0·25N, with 44 per cent. of the salt crystallising, to 1·49 for an acidity 2N, with 58·3 per cent. crystallising. The condition chosen for study was 0·5N-acidity, with 50 per cent. crystallising, for which K is 1·62. For the bromide, the value of K fell from 2·60 for 0·25N-acidity and 30 per cent. crystallising, to 2·45 for 1·0N and 38·2 per cent. crystallising. The condition chosen for further study was 0·33N-acidity and 33·3 per cent. crystallising, for which K is 2·5. The enrichment factor is independent of the relative concentration of radium or radium and mesothorium in the solution. From the second communication it appears that, so long as the same fraction of crystals separate, it is independent of acidity. As already known, the bromide offers advantages over the chloride in speed of separation, especially in the earlier stages of the separation. Some evidence was obtained of the formation of a compound, $RaBr_2,2BaBr_2,6H_2O$, as the final product of the fractionation in a weakly acid solution, corresponding with 39 per cent. of anhydrous radium bromide, which would explain the advantage of the chloride over the bromide in the later stages of the purification. On the other hand, in very strongly acid solutions, above 2N, and very small concentration of the radium, below 10^{-7}, the process is actually reversed, and more of the radium remains in the mother liquor than separates out with the crystals.

The most favourable method of carrying on the fractionation

[76] *Ann. Reports,* 1916, **13**, 249; F. Soddy, *Phil. Mag.,* 1919, [vi], **38**, 483; *A.,* 1919, ii, **443**.

in practice is by a system in which the crystals and mother liquors move one step in opposite directions in the series at each crystallisation, except for the fractions enriched above the initial concentration, the mother liquors from which move two steps. In such a system carried out continuously, representing the initial concentration as unity, the series runs as shown, the figures representing the concentrations in each unit of the system: [77]

Mother liquor ←— ←— ←— ←— ←———— —— ←—

←— 0·0016 0·008 0·04 0·20 1·0 2·3 5·0 12·3 27 —→
Crystals —→   —→   —→   —→   —→   —→   —→   —→

In another study of mesothorium–radium–barium bromides, the activities were determined by γ-ray methods. The value of K was found to vary from 2·57 with 24·3 per cent. crystallising to 1·44 with 69 per cent. crystallising.[78]

Solubility of Radium Emanation.—Two series of determinations of the solubility of radium emanation in organic solvents, for the most part, have appeared. The solubility in these is much greater in general than in aqueous liquids, and increases as the hydrocarbon character of the solvent predominates over the aqueous, rising steadily, for example, in a series of aliphatic alcohols or acids.[79] A new determination of the coefficient of diffusion of the radium emanation in water at 14° gave the value 0·82 cm. per day, which corresponds with a molecular diameter of 1·85 Å.[80] The value deduced from the space-lattice of crystals was about two-thirds of this.

γ-Activity of Thorium-D.—The conclusion that in a thorium mineral 36·3 per cent. of the γ-radiation is due to mesothorium-2 and 62·7 per cent. to thorium-D [81] has been confirmed by a comparison of the γ-activities of quantities of the two products in equilibrium with the same quantity of thorium. The γ-activity due to thorium-D was found to be 1·81 times as great as that due to mesothorium-2. Since only 35 per cent. of the thorium atoms disintegrating produce thorium-D, it follows that, atom for atom, thorium-D gives 5·17 times as much γ-radiation as mesothorium-2. From these data, a table of the changes of the γ-activity of a pure mesothorium preparation with time has been constructed. If the

[77] C. E. Scholl, *J. Amer. Chem. Soc.*, 1920, **42**, 889 ; *A.*, ii, 408.

[78] J. L. Nierman, *J. Physical Chem.*, 1920, **24**, 192 ; *A.*, ii, 408.

[79] Alfred Schultze, *Physikal. Zeitsch.*, 1920, **95**, 257 ; *A.*, ii, 577 ; G. Hofbauer, *Sitzungsber. Akad. Wiss. Wien*, 1914, **123**, 2a, 2001.

[80] E. Ramstedt, *Medd. K. Vetenskapsakad. Nobel Inst.*, 1919, **5**, No. 5 *A.*, ii, 72.   [81] *Ann. Reports*, 1918, **15**, 220.

initial activity is unity, in three years it is 1·62, and in ten years unity again.[82]

Natural Radioactivity.

Brass.—The improvements in the methods of recording the passage of individual α-particles have been applied to the excessively feeble natural radioactivity of common materials, and have thrown light on the important question whether this is wholly due to known radioactive impurities or is in any part a specific activity. A statistical examination of the α-particles emitted from a hollow brass sphere showed that a large number of the α-particles possessed a very short range, shorter than that of any of the known radio-elements. The rate of emission was one α-particle per sq. cm. of surface in 9·25 hours. The range of this new type was estimated at 1·8 cm. of air. By the Geiger-Nuttall relation, this corresponds with a period of life $1·5 \times 10^6$ times that of uranium. Hence the inference is formed that the α-particles are derived from an actual disintegration of the metal, either copper or zinc, with this excessively long period of 10^{16} years. From copper an isotope of cobalt, and from zinc an isotope of nickel, would result in an α-ray change. It is sad, however, that such elaborate and important physical experiments should be conducted on such a material as—brass!

Rocks.—A survey of the radioactivity of the rocks encountered in the piercing of the Loetschberg Tunnel, which runs from Kandersteg to Goppenstein, in the Bernese Oberland, showed unusual similarity of composition along the length of the tunnel. This agrees with the fact that no abnormal temperature gradient, such as was encountered in the St. Gothard Tunnel, was experienced. The average of all the rocks (eighty-two specimens) was $2·2(\times 10^{-12}$ grams of radium per gram). The rocks at the Kandersteg end are Jurassic limestones, in the centre Gastern granite, and, at the southern end, crystalline schists of all classes. The granites were somewhat lower in radium content, and the calcareous and schistose rocks somewhat higher, than the average for these classes.[83]

The rocks of the Kolar gold field, on the Mysore plateau, southern India, consist of schists of very uniform character, which contain as little radium as, and are probably older than, any rocks known. The temperature gradient in the mines is abnormally

[82] H. N. McCoy and G. H. Cartledge, *J. Amer. Chem. Soc.,* 1919, **41,** 42 *A.,* 1919, ii, 89.

[83] J. H. J. Poole, *Phil. Mag.,* 1920, [vi], **40,** 466 ; *A.,* ii, 657.

low. The average radium content was 0.19×10^{-12} gram per gram.[84]

Spring Waters.—A survey of sixty Canadian mineral springs, and, later, of six hot springs at Banff, Alberta, disclosed only moderate activities. The latter are the most active in Canada, and possess an emanation content of from 2 to $6(\times 10^{-10}$ curie per litre). For the escaping gases, higher values, up to 24, were obtained.[85] The springs of Colorado are exceptionally active, the emanation content for ninety-five exceeding 10, and for five 100. The most active, 305, is surpassed by few European springs.[86]

The sulphur–soda springs of Bagnères-de-Luchon have been found to be the most radioactive in France, and, apart from such waters as actually originate in uranium mines, to be exceeded in activity by less than a dozen in the whole world. The group of some twenty-four springs possessed an emanation content between 4 and 415, five being above 240, and higher than any other French springs.[87]

The principal spring at Bagnoles de l'Orne showed, over a month of observations, variations in emanation content from 2 to 15. Previous observations had given much higher values, 24 in 1907 and 113 in 1904. These variations have been traced to the rainfall. After rain, at an interval varying from six to thirteen days, the springs in this neighbourhood were found to reach a maximum emanation content, the greater the heavier the rainfall. This shows that the activity of the spring is derived from surface waters percolating through radioactive strata and mixing with the deep spring water.[88] Two papers dealing with the practical technique of such measurements have appeared.[89]

The Ocean.—The rate at which radium is supplied to the ocean by rivers and the denudation of the land cannot maintain the quantity present. It follows that there must be in sea-water uranium and ionium in equilibrium proportion to the radium. Taking the mean radium content of sea-water as 1.2×10^{-15} gram per c.c., the uranium must be 4×10^{-6} gram per litre of sea-water, or 0.1 milligram per kilogram of sea-salt. This is about one-tenth of the estimated content of gold in sea-water. On this view, no

[84] H. E. Watson and G. Pal, *J. Ind. Inst. Sci.*, 1914, **1**, 39 ; *A.*, ii, 278.

[85] J. Satterly and R. T. Elworthy, *Trans. Roy. Soc. Canada*, 1917–1918, [iii], **11**, 17, 27 ; **12**, 153 ; *A.*, 1919, ii, 41, 72, 312.

[86] O. C. Lester, *Amer. J. Sci.*, 1918, [iv], **46**, 621 ; *A.*, 1919, ii, 6.

[87] A. Lepape, *Compt. rend.*, 1920, **171**, 731 ; *A.*, ii, 727.

[88] P. Loisel, *ibid.*, 1919, **169**, 791 ; 1920, **171**, 858 ; *A.*, 1919, ii, 489 ; 1920, ii, 727.

[89] O. Nürnberger, *Physikal. Zeitsch.*, 1920, **21**, 198 ; *A.*, ii, 345 ; H Greinacher, *ibid.*, 270 ; *A.*, ii, 463

great variation of radium content with depth is to be anticipated in the ocean. It is calculated that the ocean and the land must be approximately equal factors in maintaining the amount of emanation in the atmosphere, the smaller contribution of the ocean per unit of surface being counterbalanced by its greater area.[90]

The Atmosphere.—At Innsbruck, as the result of forty-nine observations of the emanation content of the atmosphere by the charcoal method, values were obtained between 1110 and 43, with a mean of 433($\times 10^{-15}$ curie per litre), which are considerably above those found in other localities.[91]

It will be recalled that in 1912, during balloon ascents, an increase in the penetrating radiation of the atmosphere was recorded, which became considerable at the height of 3000 metres.[92] Now kite experiments, carried out at the aeronautical observatory of Lindenberg, Prussia, have shown that the active deposit on a wire under the influence of the earth's field is much greater at heights between 1000 and 2500 metres than at the surface. A study of the variations of this from July 29th to December 2nd, 1913 (ninety-eight observations), showed that strong increases occurred with the fall of the barometer. Since, at this height, the supposed explanation of the influence of the fall of the barometric pressure in facilitating the escape of emanation from the surface soil fails, the changes of activity and pressure are regarded as originating in a common cause. A clear parallelism was found to exist between the changes of the activity and what is termed the "potential temperature" of the layer of the atmosphere between 1000 and 2500 metres. By this term is meant the temperature which the air would assume if adiabatically brought to normal pressure. Presumably the changes of this function are independent of internal meteorological influences, and are a measure of the external solar influences. However that may be, temperature changes are supposed to be the cause of the pressure changes, and themselves to originate from a mass radiation from certain limited zones of the solar surface of emanation particles into the upper atmosphere, which owes to this its chief source of heat. Whatever the explanation may prove to be, the study of the radioactivity of the upper atmosphere is clearly likely to lead to important advances.[93]   FREDERICK SODDY.

[90] V. F. Hess, *Sitzungsber. Akad. Wiss. Wien,* 1918, **127**, 2*a*, 1297.
[91] R. Zlatorovic, *Wien. Anz.,* 1920, 75 ; *A.,* ii, 657.
[92] *Ann. Reports,* 1912, **9**, 327 ; 1913, **10**, 288.
[93] H. Bongards, *Physikal. Zeitsch.,* 1920, **21**, 141 ; *A.,* ii, 277.

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ERRATA.

(ANNUAL REPORTS, 1919.)

Page	Line		
110	10	} for "coumarin" read "coumaran."	
111	16		

110   10 ⎱ for "coumarin" read "coumaran."
111   16 ⎰

120   11   „   " " read " "

absence of lime, an acid condition of soil and absolute sterility; fertility, however, is restored by the use of lime. This restoration was effected by applying 2 tons per acre of lime (1897). Later experiments have been directed to seeing whether smaller quantities would suffice, and in 1905 lime was applied in smaller quantities (5 cwt., 10 cwt., and 1 ton per acre respectively) to land previously incapable (through the continued use of ammonium salts) of bearing a crop. Among the striking results may be mentioned the following :—

Manures per acre.				Wheat, 1906. Bushels Corn.	Barley, 1906. Bushels Corn.
Ammonium salts, without lime				3·4	no crop
,, ,, with 5 cwt. lime (1905)				19·2	11·6
,, ,, with 2 tons lime (1897)				26·1	25·4
Mineral manures and ammonium salts, without lime				—	1·7
,, ,, ,, ,, with 1 ton lime (1905)				—	33·9
,, ,, ,, ,, with 2 tons lime (1897)				—	44·3

Incidentally these results also show that the influence of an application of two tons of lime to the acre will last for quite nine years, the dressings put on in 1897 still showing their effects. F. Wohltmann, H. Fischer, and P. Schneider[1] state that manuring with lime increases the power of decomposing nitrogenous substances in soils, and that both nitrification and denitrification are assisted by it. M. Hoffmann[2] instances experiments extending over five years, and showing the general benefit of lime, even leguminous plants (lupins) profiting by it. R. Ulbricht,[3] however, finds that with lupins, vetches, and serradella the application of lime produces a slightly diminished assimilation of nitrogen and phosphoric acid, the magnesia in the plants being at the same time considerably increased.

Investigators in Japan have continued their inquiries into the relations of lime to magnesia in soils as affecting the yield of crops. Thus, G. Daikuhara[4] showed that the yield of barley in a soil having the ratio CaO : MgO : : 0·34 : 1 was doubled when, by the addition of calcium carbonate, the ratio was made 1 : 1. The same author, experimenting with tobacco, found that if the ratio of CaO to MgO, in a soil of 1 : 1, was increased by liming to 2 : 1 or even 4 : 1, benefit was obtained. The latter proportion corresponds to the ratio of these constituents in the ashes of tobacco. With flax and spinach S. Namikawa[5] obtained

[1] *Bied. Centr.*, 1905, **34**, 805.   [2] *Ibid.*, 1906, **35**, 12.

[3] *Landw. Versuchs-Stat.*, 1906, **63**, 321.

[4] *Bull. Imp. Centr. Agr. Exp. Stat. Japan*, 1905, **1**, 13.

[5] *Bull. Coll. Agr. Tōkyō*, 1906, **7**, 57.

the best results by making the ratio of CaO to MgO 1 : 1. On the other hand, S. Maki and S. Tanaka [1] showed that if land be over-limed, it may be benefited by adding magnesium sulphate to it. Manuring with magnesium sulphate has been tried in several instances (magnesium carbonate being difficult to obtain in Japan), and it is found that it has about seven times the efficacy of magnesite, so that when magnesium sulphate is used the ratio of CaO to MgO should be 7 : 1, whereas with magnesite it should be 1 : 1.

Interesting as these results in regard to lime and magnesia are, it has to be remembered that the experiments have been with pot-culture only, and they need the confirmation of field work. It would be very desirable to gather experience from field soils containing lime and magnesia in different relative proportions, and to ascertain if the general results obtained in pot experiments hold good in actual practice.

Phosphates.

D. N. Prianischnikoff [2] has experimented on the relative value of different phosphates. In sand culture the effect of bone meal was about 50 to 60 per cent. of that of soluble phosphates, and when a crude phosphate, like phosphorite or apatite, was used, although gramineous crops improved very little, lupins did so considerably. In sand cultures ammonia salts had the power of rendering even very sparingly soluble phosphates available for the use of plants. The same author,[3] working with aluminium phosphate and iron phosphate, found that millet, vetches, and mustard, grown in sand, would assimilate the phosphoric acid from aluminium phosphate, either when merely dried or when ignited, as also from iron phosphate if merely dried, but not if ignited. Rye and wheat, however, could not utilise the phosphoric acid of crude phosphates, although lupins did as well with crude phosphate as with bone phosphate.

Different processes have been suggested for rendering raw phosphates available for use. One of these is that of the Wolters Phosphat. Gesellschaft,[4] in which raw phosphates are melted in a Siemens' furnace with alkali silicates and lime, the product being then led into cold water, when nearly all the phosphoric acid is found to be soluble in citrate solution. The materials suggested for use are:—Tricalcium phosphate 40 per cent., silica 30 per cent., lime 14 per cent., soda 16 per cent.

[1] *Bull. Coll. Agr. Tōkyō*, 1906, **7**, 61.
[2] *Landw. Versuchs-Stat.*, 1906, **65**, 23.
[3] *Bied. Centr.*, 1905, **34**, 741.
[4] Eng. Pat. 9183, April 18, 1906.

The influence of phosphoric acid on straw has been observed by
D. Lienau and A. Stutzer,[1] who conclude that it promotes the
thickening of the cell wall. This effect is, however, greatly
diminished if much potassium, calcium, or nitrogen is present. The
smaller the amount of total ash and of potassium in the straw,
the greater will be the thickening of the cell walls; the appli-
cation of phosphates has the effect of reducing these quantities,
whilst the amount of phosphoric acid in the straw is found not
to be itself dependent on the quantity supplied as manure.

G. André[2] determined at various stages the phosphoric acid
and nitrogen in the sap of certain quickly-growing annuals (*Papaver*
and *Pyrethrum*), with the result that the nitrogen in the sap was
shown in general to diminish as the phosphoric acid increased. He
also found that in annuals a portion of the phosphoric acid
migrated, as soluble mineral phosphate, from the leaf to the
ovule, while another portion is removed in combination with
nitrogenous organic substances.

W. Windisch and W. Vogelsang[3] have investigated the nature
of the phosphoric acid that occurs in barley grain. In making a
cold-water infusion of barley they found that this contained
phosphoric acid of which a considerable portion was in the
inorganic state. But when the infusion was made in such a way
as to exclude the action of enzymes, the whole of the phosphoric
acid was found to be in the organic state, and they conclude that
raw barley contains no inorganic phosphates, but that these are
only produced when the organic compounds are, as in the steeping
and malting processes, subjected to the hydrolytic action of the
enzymes. This change goes on better in the dark.

W. Zaleski,[4] from experiments with seedlings of *Lupinus
angustifolius*, has come to the same conclusion regarding the action
of enzymes on proteins containing phosphorus, and shows that
inorganic phosphates are in this way produced.

A. D. Emmett and H. S. Grindley[5] have similarly examined the
phosphorus-containing substances in flesh, and find that in beef 75
per cent. of the total phosphorus is soluble in cold water, and
that one-fourth of this consists of organic compounds.

[1] *Landw. Versuchs.-Stat.*, 1906, **65**, 253.
[2] *Compt. rend.*, 1906, **142**, 106, 249.
[3] *Woch. Brau.*, 1906, **23**, 516.
[4] *Chem. Centr.*, 1906, ii, 893.
[5] *J. Amer. Chem. Soc.*, 1906, **28**, 25.

Availability of Phosphoric Acid in Soils.

A. D. Hall and A. Amos [1] have further investigated the means of determining the amount of plant food—especially phosphoric acid—which may be reckoned as being immediately " available " for plant food. They criticise B. Dyer's citric acid method, and point out that, although very useful, it must be regarded as purely empirical, inasmuch as it is based on the now generally abandoned theory of the excretion by roots of acids other than carbon dioxide. The American method of using a $N/200$ solution of hydrochloric acid is similarly criticised. Both leave out of account the nature of what is left in the soil, and presume that this will not in turn become " available " until the soil has undergone a further weathering process. Many circumstances, such as cultivation, the supply of water, the nature of the crop grown, &c., will cause variations in the amounts of the constituents assimilated by the crop. This has led Whitney to regard the soil water as the important matter of consideration, and as possessing a constant composition for all soils, being always in equilibrium. Hall and Amos accordingly adopted the plan of attacking the soil continuously with the solvent, removing the first portion of the solution after equilibrium had been attained. The remainder of the soil was then attacked with a fresh portion of the solvent, and so on. At first the solvent employed was carbon dioxide and water, but, because of the difficulty of filtration, and that some of the soil got into the extract, this was given up in favour of a 1 per cent. solution of citric acid. A period of twenty hours, with constant agitation, was found to suffice for the first separation, and to remove as much phosphoric acid as was extracted when the process was continued for five days. The solution was removed, the soil washed free of acid, and then again agitated with a further quantity of solvent. The calcium carbonate originally present was practically all removed in the first extraction, and no steps were taken to restore it. In the second extraction less than half the amount of phosphoric acid was removed, in the third about one-half that obtained in the second, and, finally, by the time of the sixth extraction the quantity removed by each successive treatment became constant.

Experiments were then made on the soil to which dicalcium phosphate was added, and it was ascertained that some of the phosphoric acid soluble in the citric acid was retained in the solid state by the soil. After a fourth and fifth extraction a point was reached where the compound remaining in the soil was uniform.

[1] *Trans.*, 1906, **89**, 205.

But this point of equilibrium varied in different soils, indicating differences in the nature of the phosphoric acid compounds in soil. Whitney's theory of the formation in soils of solutions of approximately constant composition, and independently of the fertilisers used, is thus not supported, and it would appear that the soil water is of varying concentration in different soils. The available phosphoric acid is shown by the sum of the phosphoric acid removed in the first four or five extractions; but as this has a constant ratio to the amount dissolved in the first extraction of twenty hours, for all practical purposes a single extraction gives as good a result as repeated ones.

G. S. Fraps[1] states that aluminium, iron, and calcium phosphates (as in phosphorite, vivianite, apatite, &c.), dissolve completely in $N/5$ hydrochloric and nitric acids under soil conditions. Conducting pot experiments with cow-peas he found that the plants removed from 17 to 60 per cent. of the phosphoric acid soluble in nitric acid, and he concluded that a relation was indicated between the phosphoric acid so dissolved and the needs of the soil.

Potash and Soda.

M. Berthelot,[2] by treating wood ashes with 1 per cent. hydrochloric acid and then washing with water, found that from 5 to 6 per cent. of the total potassium was retained as organic compounds. He also ascertained the presence of organic potassium compounds in living vegetable tissues; if digested with potassium acetate solution the insoluble organic matter fixed a certain amount of potassium, and if solution of calcium acetate was used calcium was fixed and potassium liberated.

The influence of potassium manures on the quality of barley has been studied by several observers, and, among them, O. Reimer [3] has noticed that, whilst potash increases the yield of grain, the amount of proteins is in no way reduced. K. Asô [4] obtained the same increase of grain with barley by using potassium chloride, finding, however, that potassium sulphate was more favourable to straw production; potassium silicate was, on the whole, the best form, and the new potassium manure " martellin " gave good results in this connexion. Sulphate of potash and kainite have been compared as potassium manures for potatoes at the Woburn Experimental Farm,[5] the results of 1905 confirming those

[1] *J. Amer. Chem. Soc*, 1906, **28**, 823.

[2] *Compt. rend.*, 1905, **141**, 793, 1182.

[3] *Chem. Centr.*, 1906, i, 154.

[4] *Bull. Coll. Agr. Tōkyō*, 1906, **7**, 67.

[5] *J. Roy. Agric. Soc.*, 1906, **67**, 305.

previously recorded to the effect that sulphate of potash is, on a light, sandy loam, a preferable form to kainite. 1 cwt. per acre of the former and 4 cwt. per acre of the latter being respectively used. This proved to be alike the case whether nitrate of soda or sulphate of ammonia was used as the nitrogenous manure. The relations of potassium and sodium salts in soils and as supplied in manures have occupied considerable attention, and especially in connexion with sugar-cane and sugar-beet cultivation. J. F. Breazeale [1] grew wheat plants in solutions containing all necessary elements except potassium and sodium, then removing the plants to solutions with full nutrient constituents and ascertaining the amounts of the constituents taken up. In this way it was found that potassium was taken up much more vigorously when sodium had been left out in the first period than when it was present all the time. Similarly, by taking beet plants which had been first grown in soil to which potassium or sodium salts had been given as manures, and then removing them to solutions containing full nutrient matters, the plants to which no potassium had been given to the soil for some years took up potassium more vigorously than where sodium had been applied. J. Urban [2] has studied the relation of potassium and sodium salts in the case of sugar-beet. When sodium nitrate alone was used on a sandy humus soil there was abnormal development of leaf, and though the total ash (leaf and root) was much the same as in normal beets, it contained a very high proportion of sodium salts, much exceeding that of the potassium salts. So, although sodium may replace potassium in the plant's composition, it is at the expense of proper root development and consequently of sugar-production. Urban attributes the abnormal composition to the great preponderance of nitrogen over potash, the ratio of K_2O to N having been 1 : 3·1, whereas he considers that the best ratio for sugar production is 1 : 1.

Silica.

A. D. Hall and C. G. Morrison [3] have examined again the part played by silica in the nutrition of plants, and, while confirming previous conclusions as to its not being a necessary constituent of plant food, have brought out interesting points as regards the functions which it exercises, and mainly in reference to the taking up of phosphoric acid. The observations have been made in respect of some of the permanent grass experiments in Rothamsted Park and the permanent barley plots in Hoos Field. On the grass land

[1] *J. Amer. Chem. Soc.*, 1906, **28**, 1013.

[2] *Zeit. Zuckerind. Böhm*, 1906, **30**, 397.

[3] *Proc. Roy. Soc.*, 1906, **77**, *B*, 455.

the use of sodium silicate along with mineral manures and ammo-
nium salts gives, over 42 years, an annual increase of 10 per cent. in
the crop above that of a similarly manured plot without sodium
silicate. An explanation of this is supplied by the barley plots,
where sodium silicate has been employed with and without
phosphates. Its use causes earlier formation of the grain and
hastens the ripening of the crop. The omission of both silica and
phosphoric acid results in a poor crop (27 to 28 bushels per acre),
but if sodium silicate is applied without phosphoric acid the crop
is increased to 34 to 36 bushels, and more phosphoric acid is found
in the ash of the grain, although there is less in the ash of the
straw. Silica would thus appear to be able partly to replace
phosphoric acid, the effect of it being that it imparts a stimulus
which enables more phosphoric acid to be taken up by the plant
from the soil. Barley plants were examined at different stages of
growth, and it was found that, in general, only 9 per cent. of
the silica reaches the grain in the early stages, and that, whereas
ordinarily the dry matter reaches its maximum about July 18—25,
if no silica or phosphoric acid is supplied the dry matter does
not reach its maximum until August 8. A series of water-cultures
further confirmed these results and showed that while silica cannot
replace phosphoric acid it may stimulate the plant to take up
more. And, lastly, by extracting the soil of the different plots with
hydrochloric and citric acid respectively it was shown that the
sodium silicate has no direct solvent action on the soil phosphates.

The " Rarer " Constituents of Plants and Soils.

(a) *Manganese.*

N. Passerini [1] grew lupins (*Lupinus albus*) in a soil containing
0·068 per cent. of manganese, and examined the different parts of
the plant in regard to their contents of manganese. The leaves
contained 8·26 per cent. of ash, and of this ash 12·43 per cent.
consisted of manganese reckoned as Mn_3O_8; the seed pods con-
tained the next highest proportion, namely, 6 to 7 per cent. of the
ash (total 3·5 per cent.), and then the stems and the seeds, the
roots lastly having still less. In pot experiments, with and without
addition of manganese carbonate, the soil containing only 0·0002
per cent of manganese, the dry matter contained 0·0095 of man-
ganese when none was added and 0·0636 per cent. when it was given
as manure. T. Katayama [2] showed that manganese has a stimula-
tive effect on oats, barley, rice, &c., although this is not so great

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[1] *Bol. Ist. Agrar. Scandicci*, 1905, [ii], **6**, 3.
[2] *Bull. Coll. Agric. Tōkyō*, 1906, **7**, 91.

as on leguminous plants. Using manganous sulphate on peas in quantity to supply 0·015 per cent. manganous sulphate to the soil, the increase was 50 per cent. in the yield of straw and 25 per cent. in that of the seeds, whereas with barley the total increase was only 10 per cent. Quantities much exceeding the above tended to decrease the yield. G. Salomone[1] confirms these results as to the beneficial influence of a certain quantity of manganese and the tonic action of large amounts, and points out that the manganic salts are more tonic than the manganous, manganic acid especially being hurtful. M. Nagaoka[2] obtained confirmation of former experiments, getting with rice a gain of 15 per cent. when using manganese sulphate up to 100 kilos. per hectare.

(b) *Copper.*

A. Stutzer[3] grew *Trifolium pannonicum* in pots with sand, garden soil, calcium carbonate, and mineral manures. He added to two of them finely-divided copper (1 gram and 10 grams) and to other two powdered copper oxide in the same amounts, other pots receiving no copper. In only one instance—when 10 grams of copper oxide were used—was any injury noticeable, but here the plants either failed or remained very small. Examination of the plants failed to detect copper in them, even in the roots. W. W. Skinner[4] has examined the effect on vegetation of irrigation water containing copper salts derived from the waste products of mining operations. One part of copper in 800,000 has been found to be fatal to the growth of corn, and as little as one part in 700 millions will retard the growth of wheat seedlings. The author concludes that 1 part of copper per million is enough to condemn a water for use for irrigation purposes. He has further tested the general belief that the presence of carbonates and bicarbonates, by rendering copper insoluble, will remove any danger of injury, and finds that it is not justified, inasmuch as a considerable amount of copper remains in solution, even if carbonates and bicarbonates are present in quantity. E. Bréal[5] treated seeds with a solution prepared by boiling starch in 1 litre of 0·3 per cent. of copper sulphate solution. The seeds were soaked for twenty hours and then left to dry. Their weight was increased somewhat, their germination was improved, and, besides the freedom from " smut " and other diseases, the crop was somewhat increased. (See also under mercury.)

[1] *Chem. Centr.*, 1906, ii, 532.
[2] *Bull. Coll. Agric. Tōkyō*, 1906, **7**, 77.
[3] *Landw. Versuchs-Stat.*, 1906, **65**, 285.
[4] *J. Amer. Chem. Soc.*, 1906, **28**, 361.
[5] *Compt. rend.*, 1906, **142**, 904.

(c) *Aluminium.*

H. Micheels and P. de Heen [1] investigated the effect of aluminium salts on the germination of wheat, with the result that, whilst they find alumina or kaolin to be beneficial, the addition of soluble aluminium salts is proved to be injurious. On seedlings themselves it would seem, from the work of H. D. House and W. J. Gies,[2] that the injurious effect is dependent entirely on the extent of the concentration.

(d) *Mercury and Silver.*

T. Bokorny [3] finds that algæ are killed by salts of copper, mercury, and silver if the concentration is 1 to 1 million. All other metals require to be in more concentrated solution than this to do any injury.

(e) *Iodine.*

S. Uchiyama,[4] by using small amounts of potassium iodide, increased the yield of *sesamum* and spinach. With *sesamum* he obtained an increase of 16 per cent. by using 124 grams of potassium iodide per hectare. This was confirmed by a field experiment, and the matter has some interest owing to the common practice of using seaweed as manure where available.

(f) *Fluorine.*

Experiments of K. Asō [5] with both soil and water culture seem to point to precipitated calcium fluoride as possessing some stimulating action. This cannot, however, be due to hydrogen fluoride, inasmuch as this is not liberated by carbon dioxide and weak acids.

Availability of Soil Constituents.

J. König, J. Hasenbäumer, and C. Coppenrath,[6] in seeking for a method of determining the available constituents of soils, have obtained the best results by placing the soil in a linen bag inside a copper vessel and heating the whole with water for three hours under a pressure of four atmospheres. The solution is then filtered, evaporated down, and the different constituents estimated.

[1] *Bull. Acad. roy. Belg.*, 1905, 520.
[2] *Proc. Amer. Physiol. Soc.*, 1905, xix—xx.
[3] *Chem. Zeit.*, 1905, **29**, 1201.
[4] *Bull. Imp. Centr. Agric. Exp. Stn. Japan*, 1906, **1**, 35.
[5] *Bull. Coll. Agr. Tōkyō*, 1906, **7**, 85.
[6] *Landw. Versuchs-Stat.*, 1906, **63**, 471.

Oxidation in Soils.

E. J. Russell[1] has continued his work on the rate of oxidation in soils and the relation this bears to their productiveness. Oxidation is due mainly, but not exclusively, to the action of microorganisms, as it still goes on when the soil has been sterilised by heating or by treatment with mercuric chloride or other re-agents. The rate of oxidation is, however, much reduced. More-over, it does not depend on the amount of organic matter present; up to a point the presence of moisture helps; similarly, the pre-sence of calcium carbonate or of a carbohydrate aids the rate. With partial sterilisation the rate of oxidation also increases, and this would lead to the belief that, whilst the work of some organisms is checked, the activity of others may be favourably influenced by partial sterilisation. This only takes place, however, under aërobic conditions, as in arable soils, but not in pasture soils, where the conditions are anaërobic.

C. Schulze[2] has investigated the effect of sterilisation of soils, and finds that whilst some substances injurious to plants are formed, the soil constituents generally are made more available. The result as regards the plant will depend on the predominance of one or the other influence.

It is clear from the foregoing and the observations of others, that there remains still a great deal of work to be done in ascertaining exactly what changes take place in the bacterial and chemical con-ditions of different soils as well as in their physical relations, through the employment of processes of sterilisation, partial or complete, and that the results obtained with sterilised soils have to be taken in conjunction with the various changes thereby pro-duced.

Germination.

P. Becquerel[3] has studied the action of carbon dioxide on seeds which have been decorticated or perforated. When the seeds are in their naturally dry condition they will not be injured, though kept in an atmosphere of carbon dioxide; but if they are previously immersed in water for a quarter of an hour they will be all killed by exposing them to an atmosphere of carbon dioxide. O. Kamberský,[4] by placing seeds for forty-eight hours in contact with a nutritive solution containing ammonium nitrate, potassium

[1] *Brit. Assoc. Reports* (Section *B*), *York,* 1906.
[2] *Landw. Versuchs-Stat.,* 1906, **65,** 137.
[3] *Compt. rend.,* 1906, **142,** 843.
[4] *Chem. Centr.,* 1906, i, 570.

nitrate, di-ammonium hydrogen phosphate, and di-sodium hydrogen phosphate (Iszleib's solution), found that germination was retarded and a lower germination percentage obtained. A. Stutzer [1] has shown also that nitrates generally act injuriously on germinating seeds; beet plants are very sensitive to nitrates, but red clover resists their action. The behaviour of cyanamide towards germinating seeds has already been dealt with (page 261), but Bartsch [2] has shown that, while the germination of mustard, oats, and barley is affected when the seeds are sown at the time of applying the cyanamide, and will be still noticeable if a week intervenes, yet, if an interval of three weeks is allowed between the application of the cyanamide and the sowing of the seed no injurious action will follow.

H. Micheels and P. de Heen [3] have further found that ozone has an injurious effect on seedlings, the roots in particular being attacked.

Assimilation.

F. L. Usher and J. H. Priestley [4] show that, in presence of chlorophyll and under suitable conditions, aqueous carbon dioxide is decomposed into formaldehyde and hydrogen peroxide, formic acid being produced as an intermediate substance. This goes on independently of any enzyme action, and depends solely on the proper physical and chemical conditions being present. It is possible to reconstruct this process outside the green plant. The formaldehyde and hydrogen peroxide rapidly undergo change, and are not found in the assimilating leaf under ordinary conditions. Working on the leaves of *Acer Negundo,* B. Schultze [5] ascertained that the increase in weight of the leaves, under the influence of light, was not due only to the assimilation of starch, but also to that of proteins. But while carbon assimilation went on the production of proteins gradually diminished.

Development.

By growing green plants without carbon dioxide in an artificial soil containing amides, J. Lefèvre [6] showed that the dry matter of the plants rapidly increases, the growth being quite normal. In absence of light the plants failed altogether, although amides were present. The results go to show that the carbon dioxide of the soil is not absorbed by the roots, or, at least, is not utilised by them.

The oxidising power of living cells on the surface of roots was

[1] *J. Landw.*, 1906, **54**, 125. [2] *Chem. Centr.*, 1906, i, 585,
[3] *Bull. Acad. roy. Belg.*, 1906, 364. [4] *Proc. Roy. Soc.*, 1906, **78**, *B*, 318.
[5] *Bied. Centr.*, 1906, **35**, 35. [6] *Compt. rend.*, 1905, **141** 664, 834, 1035.

shown by experiments of M. Raciborski,[1] who grew plants in solutions which do not affect the life of the roots' cells. but which, on oxidation, yield products either themselves coloured or capable of colouring suitable reagents. This power is, however, a purely local one, and is confined to the absorbent surfaces of the roots, being strongest near the root hairs.

The influence of light on the development of proteins in the wheat grain has been studied by J. Dumont.[2] The accumulation was greatest under the influence of brown light, then under green, blue, and red light successively. In the absence of light, A. Kiesel[3] found not only asparagine to increase, but also other amino-acids, especially leucine, and certain bases, such as arginine. not found in healthy plants.

H. Schjerning,[4] in investigating the formation and changes in the protein substances of barley during growth, ripening, and storing, concludes that barley has attained its full maturity when the soluble carbohydrates are converted into insoluble ones and the soluble into insoluble proteins. H. T. Brown, F. Escombe, A. McMullen, and J. H. Millar[5] have observed the migration of nitrogen in barley from the endosperm to the embryo during germination. It was noticed by them that if the embryo was removed and allowed to grow in water or in a carbohydrate medium the root exhibited a restricted development, and the embryo seemed to be suffering from nitrogenous starvation. This nitrogen it would, in the ordinary course, derive from the endosperm. The observation was continued to barley undergoing the malting process, the nitrogen being determined at various intervals in the endosperm, embryo, rootlets, &c. It was found that after nine days' germination 35 per cent. of the nitrogen originally present in the endosperm had migrated to the embryo, and must in so doing have been converted from the insoluble protein form into soluble and diffusible compounds.

The same authors continued their studies on the nitrogenous constituents of malt that are soluble in cold water, with a view to ascertaining how far the quality of barley depends on these. An examination of the sprouted " culms " led to the identification in them of asparagine, allantoin, betaine, and choline. The water-soluble uncoagulable nitrogens of malt have now been divided by the authors into six classes of bodies, and their approximate percentages have been also worked out. They consist of the

[1] *Bull. Acad. Sci. Cracow*, 1905, 338.   [2] *Compt. rend.*, 1905, **141**, 686.

[3] *Zeit. physiol. Chem.*, 1906, **49**, 12.

[4] *Trav. Laborat. Carlsberg*, 1906, **6**, 229.

[5] *Trans. Guinness Research Lab.*, 1906, **1**, part 2, 149, 169, 175, 238, 242, 284, 338.

following:—ammonia-nitrogen, 3·5 per cent; malt-albumose nitrogen, 20 per cent.; malt-peptone nitrogen, 31 per cent.; amide and amino-nitrogen, 8·5 per cent.; nitrogen due to organic bases, 4 per cent.; uninvestigated bodies, 33 per cent. The conclusion is also arrived at that, from the chemical point of view, no distinction can be drawn between animal and plant proteins.

The action of light on the transformation of sugars in young plants has been studied by W. Lubimenko[1] in connexion with the embryos of *Pinus pinea*. When these were exposed to light of varying intensity in sterilised solutions of sucrose, dextrose, maltose, lactose, galactose, and arabinose, it was found that under the action of the light the absorption of sucrose, dextrose, and arabinose went on, but with varying activity, diminishing as the intensity of the light increased. The light had no effect on the assimilation of maltose, lactose, lævulose or galactose.

According to G. A. Calabresi[2] pentosans would seem to be formed in young plants, but to decrease later on. In sugar-beet, when pentosans are high in amount sucrose is low, and, generally, in plants the pentosans are higher when nutritive constituents are low.

W. Palladin and S. Kostytschew[3] show that during the anaërobic respiration of seeds and seedlings a considerable amount of alcohol is formed. Both living and frozen seeds have been experimented with; with frozen peas alcohol is formed whether oxygen be present or not, but with living peas the formation of alcohol only goes on in absence of oxygen. Acetone is also found to be formed during anaërobic respiration.

W. D. Bigelow, H. C. Gore, and B. J. Howard[4] have investigated the changes which go on during ripening in certain plants containing a good deal of tannin. They find that the tannin disappears during the ripening, passing possibly into insoluble forms. Microscopical examination shows that at first the tannin is fairly uniformly distributed through the fruit, but that, as ripening proceeds, it becomes deposited in insoluble form in special cells.

Micro-organisms.

N. L. Söhngen[5] was led, by the consideration that methane, although so abundantly produced, is yet found only in traces in the atmosphere, to search for organisms which were capable of feeding on the hydrocarbon. He found that if a culture-liquid

[1] *Compt. rend.*, 1906, **143**, 516. [2] *Chem. Centr.*, 1906, ii, 964.
[3] *Zeit. physiol. Chem.*, 1906, **48**, 214. [4] *J. Amer. Chem. Soc.*, 1906, **28**, 688.
[5] *Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 327.

was impregnated with garden soil, sewage or the like, in an atmosphere of methane and oxygen at 38°, a slimy, pink film formed on the surface, and that this consisted of short, rod-like bacteria, which he named *Bacillus methanicus*. Within a week the methane is nearly all absorbed, being thus utilised as a source of carbon. H. Kaserer,[1] working on the same subject, shows that the presence of hydrogen and methane hinders the production of nitrites from ammonium salts. If there is a plentiful aëration, both oxidation of hydrogen and nitrification may go on together, but, if aëration be imperfect, nitrification will only begin after all the hydrogen has been oxidised. V. Omeliansky[2] finds that methane is produced by fermentation from cellulose, gelatin, peptone, and many other substances, and thinks it probable that all soils that have organic matter will produce methane. Accordingly, it is not possible to say, from the mere fact of methane being produced, what the nature of the organic matter decomposed is. From the excrements of pigeons C. Ulpiani and M. Cingolani[3] have isolated a microorganism which decomposes guanine into carbamide, guanidine, and carbon dioxide.

In the fermentation of sugar-cane juice C. A. Browne[4] has noticed that a frequent fermentation is that resulting in the formation of cellulose. This he has investigated and finds it to be aërobic, being due probably to *Bacterium xylinum*. From cane juice the amount of cellulose thus formed may be 7 per cent. of the total sugar fermented.

The effect of light on bacteria has been investigated by H. Thiele and K. Wolf.[5] While the bacteria were destroyed quickly by strong light, if the light was filtered through solutions of nitrates or oxalic acid it had no effect on the bacteria; if passed through disodium phosphate and potassium thiocyanate solutions enough active light passed through to kill the bacteria. From this the active bactericidal region was fixed. Light filtered through a piece of blue rock-salt crystal (the ultra-violet rays alone passing through) rapidly destroyed the bacteria.

W. Hoffmann[6] has observed the action of carbon dioxide at high pressure on the bacteria contained in river water and in milk. Under a pressure of 50 atmospheres the bacteria are killed entirely in twenty-four hours in the case of river water. But with milk the bacteria are not entirely destroyed, even at a temperature of 50°, although the casein is coagulated and separates out.

[1] *Centr. Bakt. Par.*, 1905, ii, **15**, 573.   [2] *Ibid*, 1906, ii, **15**, 673.
[3] *Atti R. Accad. Lincei*, 1905, **14**, ii, 596.   [4] *J. Amer. Chem. Soc.*, 1906, **28**, 453.
[5] *Arch. Hygiene*, 1906, **57**, 29.
[6] *Sixth Int. Congr. Appl. Chem., Chem. Zeit.*, 1906, **30**, 422.

Enzymes.

J. Stoklasa [1] has isolated several enzymes from beetroot. These he identified as oxydases, invertase and glycolytic enzymes. The latter set up alcoholic fermentation in dextrose solutions, alcohol and carbon dioxide, as well as small quantities of acetic and lactic acids being produced. Formic acid has also been found as a product, and the author hints that this may give rise to the hydrogen which is evolved together with carbon dioxide, and may play a part in the assimilation of carbon in the chlorophyll cells, in which process formaldehyde and water are formed. The glycolytic enzymes are given as (a) lactolase, (b) alcoholase, (c) acetolase (d) formilase, these causing the production of lactic acid, alcohol, acetic acid, and formic acid respectively.

C. A. Browne [2] finds invertase in the green tops of sugar-cane, and notes that if the tops are removed when the cane is cut the diffusion of the enzyme into the stalk is prevented, and there is less loss of sucrose. The darkening which sugar-cane juice undergoes after expression is due to oxydases.

Glucosides and Cyanogenesis.

Several investigators have continued their inquiries into the presence in various plants of certain glucosides which, under the action of an enzyme, gives rise to the production of hydrocyanic acid. Numerous plants other than *Phaseolus lunatus* (with which Dunstan and Henry worked) have been found to contain glucosides of this character, and the yield of hydrocyanic acid has been quantitatively recorded. W. R. Dunstan, T. A. Henry, and S. J. M. Auld [3] find *phaseolunatin* in small amount in flax seed, and an enzyme of the emulsin type similar to that in *Phaseolus lunatus*. They also find a glucoside and an enzyme similar to, if not identical with, those of *Phaseolus lunatus,* in the root of bitter cassava. L. Guignard [4] also establishes the presence of cyanogenetic glucosides in many of the Rosaceæ. He has further determined the amount of hydrocyanic acid obtained from the ground beans of *Phaseolus lunatus,* obtaining 0·052 to 0·102 per cent. with Java beans, but considerably less with Burmah, Madagascar, and Provence varieties. Further, he does not find, as others have done, that the white cultivated beans are quite free from hydrocyanic acid, and, in

[1] *Sixth Int. Congr. Appl. Chem., Chem Zeit.,* 1906, **30**, 422.

[2] *J. Amer. Chem. Soc.,* 1906, **28**, 453.

[3] *Proc. Roy. Soc.,* 1906, **78**, *B*, 145 and 152.

[4] *Compt. rend.,* 1906, **143**, 451, and **142**, 545.

examining white beans that occur among Java beans he obtains just as much hydrocyanic acid from them as from coloured beans. He states that the poisonous properties are not removed on boiling, as this only destroys the enzyme and not the glucoside. R. R. Tatlock and R. T. Thomson [1] obtained from Java beans from 0·027 to 0·137 per cent. of hydrocyanic acid. They examined separately the variously coloured beans, but could arrive at no generalisation as to the relation of colour to yield of acid. Discussing the statement that has been made that cyanogen is in the husk and not in the kernel, they state that this is not the case, but that the kernel has ten times as much as the husk. They examined several different varieties of beans, but only found hydrocyanic acid to be produced from Java beans and Rangoon beans. On steeping the beans in warm water and boiling them thoroughly, an original percentage of 0·009 of hydrocyanic acid falls to 0·002 and the enzyme is destroyed; in cold water the cyanogenetic glucoside is decomposed.

Kohn-Abrest [2] disagrees with the conclusion of Dunstan and Henry that there is one cyanogenetic glucoside in *Phaseolus lunatus*, and considers that many are present. J. W. Leather [3] examining a sample of *sorghum (Sorghum vulgare)* fodder which had proved harmful to cattle in India, found it to be immature and to contain 1·28 grains of hydrocyanic acid per lb. of green stuff. The largest quantity was found in the leaves. If left to mature the plant contained no hydrocyanic acid, but drying the immature fodder in the sun produced no change in quantity. The glucoside present was *dhurrin*, as previously recognised by Dunstan and Henry. Leather confirms the presence of hydrocyanic acid in Rangoon beans and immature linseed.

Foods and Feeding.

K. Farnsteiner, K. Lendrich, and P. Buttenberg [4] examined lards obtained from pigs that had been fed on potatoes, maize meal, cotton-seed meal, &c., with the result that a portion of the oil derived from the foods was shown to be deposited in the body fat of the animal. This was especially marked in the case of maize meal. The decomposition of foods in the absence of air has been investigated by J. König, A. Spieckermann, and H. Kuttenkeuler,[5] who find it to be practically the same in nature as when oxygen is present, although the products are different in quantity. The greatest loss is in the non-nitrogenous extract, although when air

[1] *Analyst*, 1906, **31**, 249. [2] *Compt. rend.*, 1906, **143**, 182.
[3] *Agric. J. of India*, 1906, **1**, 220. [4] *Zeit. Nahr. Genussm.*, 1906, **11**, 1.
[5] *Ibid.*, 1906, **11**, 177.

is absent there is comparatively little loss of dry matter. The loss of nitrogen is very small, the proteins decomposing only slightly. The foods, in absence of air, tend to become strongly acid, but do not alter their appearance.

E. Schulze,[1] taking potatoes, as containing a relatively large amount of asparagine, shows that this is converted, when consumed by animals, into amino-acids and then into succinic or malic acids, which have no value for fat production in the case of carnivorous animals. O. Kellner,[2] however, from experiments with sheep, concludes that asparagine may indirectly economise proteins in the case of ruminants. Lactic acid he finds to be simply oxidised and to produce heat only.

J. König [3] has attempted to separate the various constituents making up the so-called " crude fibre " in foods, and gives methods of ascertaining the cellulose, lignin, and cutin. Lignin is separated by digestion in the cold with hydrogen peroxide in presence of aqueous ammonia, it being converted by this treatment into soluble products. Cellulose is next separated from cutin by treatment with copper-ammonium hydroxide, it being thereby dissolved, leaving the cutin undissolved. As the plant gets older the lignin increases more than the cellulose, and, broadly speaking, the higher the percentage of lignin and cutin the lower is the digestibility of the crude fibre.

J. Hendrick,[4] following up the work of T. B. Wood, R. A. Berry, and S. H. Collins (see *Annual Report*, 1905, 264) has obtained similar results for yellow swedes and turnips grown in the N.E. of Scotland. He finds marked variations according as the roots are grown in different parts of the country, and emphasises (as did the authors named) the necessity of taking a large number of roots (100 suggested) in order to get satisfactory results. He has made the attempt to arrive at the value of the roots by comparing the ratio of the soluble to the insoluble matter in the solid matter of the roots.

Crops.

(a) "Strength" in Wheat.

This subject has been further attacked both from the chemical and the biological side. A. D. Hall [5] has examined critically the different constituents of the grain, with the view of finding out to which of them the quality of " strength " may be due. But he does not find any consistent correspondence between the pre-

[1] *J. Landw.*, 1906, 54, 65.   [2] *Bied. Centr.*, 1906, 35, 45.

[3] *Zeit. Nahr. Genussm.*, 1906, 12, 385.

[4] *Trans. High. and Agric. Soc. of Scotland*, 1906.

[5] *Rep. Home-grown Wheat Committee (Millers' Gazette)*, 1906.

dominance of any of these and the possession of " strength," and is unable to go beyond the general statement that nitrogen may, as a rule, be taken as a test of "strength," whilst the carbohydrate matters do not contribute to it. Hall finds that different stages of ripeness do not determine " strength," inasmuch as a crop cut dead ripe may be just as " strong " as one cut green. Nor does it follow that a highly nitrogenous grain is of necessity a "strong" one; some were, indeed, the weakest of all from a baker's point of view. But it was observed that these, if kept, became changed; their physical structure seemed to be altered, and they were then increased in " strength." Hall remarks on the observed " acidity " of flour, and finds that this is due to the presence of a little potassium phosphate.

Meanwhile the subject has been investigated further from the biological side by R. H. Biffen [1] and with more hopeful prospects. Biffen eliminates climatic conditions as having little or no bearing on the question, and attributes the whole to the matter of " selection," and looks to the producing of " hybrids " to obtain the desired quality of "strength " combined with good yield.

(b) *Quality in Barley.*

The results obtained at the Woburn Experimental Farm for the years 1898—1904 on the influence of manures as affecting the yield and quality of barley have been collected and summarised, [2] and, in general, confirm the results obtained at the Rothamsted Experimental Station. The main points as regards quality are that this was improved by mineral manuring (superphosphate with sulphates of potash, soda, and magnesia), that farmyard manure gave very variable results, and that the best ones were obtained with mineral manures in combination with ammonium salts or nitrate of soda used in moderate quantities. Nitrate of soda by itself or used in excess gave a low " weight per bushel " and much " tail " corn.

Industries.

(a) *Sugar.*

A considerable impulse has been given of late to the growing of sugar, more particularly of cane-sugar, and with this has come an extension of inquiry into points connected with the cultivation of the crop and the securing of the produce.

H. W. Wiley [3] summarises his observations on the influence of environment on sugar production in the beet. Temperature he

[1] *J. Agric. Sci.*, 1907, **2**, 1.   [2] *J. Fed. Inst. Brewing*, 1906, **12**, 408.
[3] *U.S.A. Dept. Agric. Bull.*, 1905, 96.

finds to be of the greatest importance; there is little relation between sunshine and sugar yield, but longer daylight means more sugar; rainfall only incidentally affects the output, but a small yield of crop means an increased sugar percentage; lastly, the juice becomes purer as the percentage of sugar rises.

H. and L. Pellet [1] find that sucrose is not uniformly distributed through the beetroot; some cells contain only water and salts, and the water is that termed by Scheibler "colloidal" water. Hence the difficulty in obtaining representative samples. Complete diffusion of the juices only takes place when the pulp is finely ground and digested with cold water or hot alcohol.

K. Andrlík and J. Urban [2] have examined the "objectionable" nitrogenous constituents in beet-root juice, and find that these are not amide or ammonium compounds. About 70 per cent. of the whole of the injurious matters originally present in the root are found in the juice. This quantity is increased by storage of the roots, probably owing to a breaking-down of the proteins.

Experiments in sugar-beet growing in the eastern counties of England [3] have given in 1906 an average yield per acre of fourteen tons of roots, containing 16 per cent. of sugar, with a coefficient of purity 87. This yield, however, is not sufficient, in the circumstances of this country, to "pay" for the manufacture of sugar. W. D. Horne [4] has inquired into the deterioration which sugar-cane undergoes when the canes have been cut. On each of six successive days he cut off pieces from canes, and noticed that the deterioration was greater with the top part of the cane than the bottom, but there was also a deterioration due to keeping. Thus, starting with 16·97 per cent. of sucrose on the first day, by the time the fifth day was reached the sucrose had fallen to 11·86 per cent.; in the first day there was a deterioration of 0·25 per cent., in the next two of 1·75 per cent., and in the next two of nearly 4 per cent. F. Watts and H. A. Tempany [5] observed the changes which sugar-cane juice undergoes when allowed to ferment spontaneously; the juice becomes acid and of a yellow colour, a dark scum rising to the surface; alcoholic fermentation sets in, carbon dioxide is given off, and quite 8 per cent. of alcohol is formed. Then acidification of the alcohol ensues, "cane sugar" being obtained. The acidification of the juice was found to be produced by oxidation of the sugar by bacterial agency; this could be prevented by the addition of 2 per cent. of phenol to the juice.

[1] *Bull. Assoc. Chim. Sucr. Dist.*, 1906, **24**, 615.
[2] *Zeit. Zuckerind. Böhm.*, 1906, **30**, 282.
[3] *Rep. E. Suffolk Chamber of Agriculture*, 1907.
[4] *J. Soc. Chem. Ind.*, 1906, **25**, 161.
[5] *West Ind. Bull.*, 1906, **6**, 387.

C. A. Browne,[1] jun., attributes the gradual inversion of the sucrose after the cane has been cut to the invertase which exists in the green tops of the cane. He has investigated the different fermentations, aërobic and anaërobic, which take place in the juice. Among the former are those due to *Bacterium xylinum* and to *citromyces*, and among the latter that produced by *Leuconostoc*, a viscous fermentation.

H. Pellet [2] refers to the suggestion of adding invert-sugar to molasses to aid crystallisation of the latter, since sucrose is less soluble in invert-sugar solution than in water, but he shows that this is not an advantage, inasmuch as the invert-sugar brings about the retention of more water, and this more than neutralises the benefit that might accrue.

(b) *Tea.*

H. H. Mann[3] in a paper entitled "The Fermentation of Tea" (part I.) gives a valuable contribution to our scientific knowledge of the manufacture of tea. Indeed, it may be taken, in conjunction with his earlier paper, "The Ferment of the Tea Leaf" (see *Annual Report*, 1904, 215) as supplying the first clear exposition of the scientific side of the subject. Moreover, it affords a most useful example of how the study of the underlying chemical principles can be made to contribute to the practical well-being of an important industry. Mann had shown in his earlier paper that the fermentation is due to an enzyme of the nature of an oxydase, and that the quantity in which it is present is an indication of the quality of the tea. He now goes on to consider the various constituents of the leaf, to observe the changes in them during the different processes of withering, rolling, &c., and to see in what way these affect the value of tea as a finished product. Living organisms, it is shown, do not take part in the fermentation, and their exclusion as far as possible from the fermenting room should be secured. The constituents studied in detail are (1) essential oil, (2) caffeine (or theine), (3) tannin. The quantity of essential oil present is very small; it is driven off at a high temperature, and changes into a resin on exposure to air; it seems to be one of the chief factors in determining flavour in tea. Caffeine exists to the extent of 3 to 5 per cent. Its presence has no bearing on the market value of tea, although it may have on its medical value. Mann next deals very fully with the matter of tannin, and shows that, contrary to general opinion, this is not an objectionable feature, but that there is a close connexion between the quantity

[1] *J. Amer. Chem. Soc.*, 1906, **28**, 453.

[2] *Bull. Assoc. Chim. Sucr. Dist.*, 1906, **24**, 669.

[3] *Indian Tea Assoc.*, 1906, **1** and **2**.

of tannin that can be removed in a five minutes' extraction with boiling water and the value of tea in the market. Tannin, as it occurs in the leaf, seems to be combined with sugar, and the tannin undergoes oxidation during fermentation of the leaf, through the presence of the oxidising enzyme. The oxidised tannin will then combine with the caffeine and other materials to form fresh substances which are mostly insoluble in water. During the process of rolling, the soluble matter in the leaf is reduced, and so is the amount of soluble tannin. Mann has further noticed the influence of light on the fermentation of tea, and finds that, whilst fermentation proceeds rather less rapidly with a blue light, there is no change in the percentage of tannin, but only in that of total soluble matter. What is of importance, however, is thickness of spreading, and this should not exceed $1\frac{1}{2}$ inches in depth. Experiments in green-manuring for tea established the usefulness of leguminous plants, especially *sau* (*Albizzia stipulata*).

(c) *Tobacco*.

J. Toth[1] has set out a new method of determining the organic acids in tobacco. Expressing these in terms of oxalic acid, he finds the quantity to range from 3·6 to 8·7 per cent., and, after trials with 32 different samples, concluded that bad-burning tobacco was that which contained the most organic acids, and *vice versâ*.

(d) *Cinchona*.

D. Howard[2] shows that by careful selection and cultivation the amount of quinine alkaloid in cinchona bark has been raised in Java from 4 per cent. to 10 per cent.

(e) *Cassava*.

H. H. Cousins[3] has estimated the amounts of starch obtained at different periods of growth from 23 varieties of cassava, grown in Jamaica. He gives the produce of starch per one tenth acre as follows:—At 12 months, $3\frac{1}{2}$ tons; at 15 months, $5\frac{1}{2}$ tons; at 21 months, $7\frac{1}{4}$ tons.

(f) *Eggs*.

J. Hendrick[4] has examined the composition of eggs preserved by the use of "water-glass"; he finds that there is a slow deposition of silica in the shell, but that there is no change in the composition of the interior portion.

[1] *Chem. Zeit.*, 1906, **30**, 57.   [2] *J. Soc. Chem. Ind.*, 1906, **25**, 97.
[3] *Jamaica Gazette*, Nov. 22nd, 1906, 330.   [4] *J. Agric. Sci.*, 1907, **2**, 100.

(g) *Milk*.

H. D. Richmond[1] gives this annual statement of the composition of milk, as obtained from good dairy farms supplying milk daily to London, during 1905. The figures are taken from an average of nearly 15,000 samples, and are as follows:—Fat, 3·73 per cent.; solids-not-fat, 8·97 per cent.; total solids, 12·70 per cent.; sp. gr., 1·0323. The average percentage of fat of the morning milk alone was 3·54; of the evening milk, 3·91. These figures differ but very slightly from those of 1904.

A. Morgen, C. Beger, and G. Fingerling[2] have investigated, over a period of six years, the effect of adding fat, protein matter, carbo-hydrates, &c., to foods deficient in these several constituents. By adding fat they found the yield of milk and the amount of fat in it to be both increased, but by adding protein matter only the yield was affected favourably, but not the fat. The yield of milk was, however, increased more by adding a protein than by the addition of fat. The addition of carbohydrates also had no effect on the production of milk-fat. The authors conclude that fat alone has a specific action on the production of milk-fat. Further experiments with emulsified fats showed these to possess no advantage.

Von Soxhlet[3] has observed the coagulation taking place in the case of milk that is faintly acid. At first a coagulum is formed on boiling, and this takes place when only one-eighth of the acid necessary to produce coagulation at the ordinary temperature is present. The coagulation is due to the formation of an insoluble compound of caseinogen and calcium salts.

F. Bordas,[4] by exposing milk to an atmosphere containing for-maldehyde, has found that air containing as little formaldehyde as 1 part in 100,000 will give the reaction for formaldehyde, although the milk may have been exposed for only a few minutes.

J. AUGUSTUS VOELCKER.

[1] *Analyst,* 1906, **31**, 176.   [2] *Landw. Versuchs-Stat.,* 1906, **64**, 93, 249.
[3] *Chem. Centr.,* 1906, i, 579.   [4] *Compt. rend.,* 1906, **142**, 1201.

MINERALOGICAL CHEMISTRY.

It is impossible to begin a report on the progress of Mineralogical Chemistry during the past year without making brief reference to the great loss this branch of science has sustained in the untimely death of S. L. Penfield. Equally happy as a theorist and as an experimenter, he has left in his work an enduring monument behind him. A sympathetic biographical notice, accompanied by a bibliography, has been contributed by L. V. Pirrson [1] to the pages of the *American Journal of Science.* In the person of H. A. Ward, America has also lost a veteran who, by his untiring energy as a collector, did good service in advancing our knowledge of meteorites. By the death of W. Meyerhoffer at the early age of forty-two, van't Hoff has been deprived of a fellow-worker and our science of one who did much to introduce to mineralogists and petrologists those ideas and methods of physical chemistry, the application of which promises such rich results in the future. It is, in fact, along these lines that the most important work has been done during the past year, and it is therefore fitting that this branch of the subject should occupy the first place in our survey.

General and Physical Chemistry of Minerals.

Salt Deposits.—J. H. van't Hoff [2] and his pupils have carried on their investigations with unabated energy. Number xlvi of the "Researches on the Formation of Oceanic Salt Deposits" appeared early in the year, and was devoted to a discussion of the conditions of occurrence at 83° of anhydrite, $CaSO_4$, syngenite, $CaK_2(SO_4)_2,H_2O$, glauberite, $CaNa_2(SO_4)_2$, and penta-salt, $Ca_5K_2(SO_4)_6,H_2O$; the formation of calcium chloride and tachhydrite, $CaCl_2,2MgCl_2,12H_2O$, were also considered. In number xlvii the examination of the naturally occurring calcium compounds was brought to a conclusion by a study of the relations at 83° of the triple sulphates, polyhalite, $Ca_2K_2Mg(SO_4)_4,2H_2O$, and krugite, $Ca_4K_2Mg(SO_4)_6,2H_2O$.

Work on the borates was begun last year, and the relations of

[1] *Amer. J. Sci.*, 1906, [iv], **22**, 353.
[2] *Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 218, 412, 566, 653, 689.

tincal and octahedral borax elucidated. The more difficult and complex problem presented by the double borates of calcium and magnesium with a univalent ion has now been attacked, and the range of existence and the dissociation of $NaCaB_5O_9,8H_2O$ boronatrocalcite fully determined.

It has been shown in number xlviii that this substance splits into the individual borates at about 85°, and that it probably was not formed in nature at a temperature higher than 70°. Incidentally pandermite, $Ca_3B_{20}O_{38},15H_2O$, was prepared artificially for the first time, together with a new substance, tricalcium borate, $Ca_3B_{10}O_{18},9H_2O$, not as yet observed as a mineral. The mutual transformations of the hydrates of calcium monoborate, CaB_2O_4, are the subject of a separate paper; and number xlix of the series is concerned with the conditions for the artificial preparation of colemanite, $(CaO)_2(B_2O_3)_3,5H_2O$, which it is shown can be formed from the corresponding heptahydrate and sodium chloride at 83°, or from boronatrocalcite in the same medium at 70°.

Mutual Relation of Fused Silicates.—The past year has witnessed great activity in this line of research, and the entry of American workers into the field has resulted in a notable increase of our knowledge of the calcium and magnesium silicates. In the first place, E. T. Allen and W. P. White [1] have succeeded in preparing artificial wollastonite having properties identical with those of the natural mineral, and have also made a careful examination of the hexagonal calcium metasilicate, termed by them *pseudo-wollastonite*, and of the relations between these two substances. They find that wollastonite can be readily obtained from the glass made by melting, together, at a temperature of over 1500°, molecular proportions of quartz and calcium carbonate in a platinum crucible, which is then rapidly chilled by placing it in water. On heating this glass to about 800° to 1000° it crystallises directly and rapidly into wollastonite, identified by its optical characters. The specific gravity is 2·915. When heated to about 1180° wollastonite changes into pseudowollastonite. This change is an enantiotropic one, and under proper conditions reversible. The point of transformation was determined by heating wollastonite in contact with the other form for definite periods at various temperatures, and also by observing the rate of rise of temperature as heat was supplied to the mass, a slight absorption of heat being noticed at the transition point. The volume change accompanying the transformation is so slight that it is doubtful which is the denser form. The reverse transformation is not so easily effected, and does not take place when the two forms are merely heated in contact at temperatures between 900° and 1100°, even if the

[1] *Amer. J. Sci.*, 1906, [iv], **21**, 89.

heating be continued for many hours. It can, however, be brought about by the aid of a solvent. Calcium vanadate proved suitable, and it was found that the change into wollastonite was complete if 5 grams of the silicate were heated with 1 gram of the vanadate for some days at a temperature of 800° to 900°. Beautiful transparent crystals were produced in this way. Analysis proved them to be nearly pure $CaSiO_3$, and the mean specific gravity 2·913, crystallographic characters [1] and optical properties, agreed with those of wollastonite. This inversion also takes place readily in mixtures containing excess of lime or silica, as shown by Day and Shepherd. Pseudo-wollastonite is usually considered to be hexagonal, but F. E. Wright, who has made a careful optical study of Allen and White's preparations, thinks that it is more probably pseudo-hexagonal, its real symmetry being that of the monoclinic system. The melting point is 1512°, and on cooling the liquid almost invariably crystallises above 1200° as pseudo-wollastonite. The fact that the transformation takes place at 1180° has an important geological bearing, for it fixes an upper limit of temperature above which wollastonite cannot possibly have been formed, and neither pseudo-wollastonite nor paramorphs of wollastonite after pseudo-wollastonite have been met with in nature.

The work on wollastonite has been extended by A. L. Day and E. S. Shepherd [2] to embrace the whole series of combinations of lime and silica. They began by studying the properties of the two oxides. The melting point of lime is too high for any satisfactory measurements to be made. It can, however, be fused in the electric furnace, and on cooling crystallises with well-marked cubic structure. The mean specific gravity is 3·316 at 25°. Silica, either in the form of quartz, glass, or precipitated silica, when heated for a sufficient length of time at temperatures above 1000°, changes into tridymite. The change proceeds most rapidly in the case of the precipitated silica, a fine state of division being favourable to the transformation. In order to determine the transformation temperature as accurately as possible, quartz-glass was heated with vanadic acid, sodium tungstate, or a mixture of 80 per cent. potassium chloride with 20 per cent. lithium chloride. Below 760° quartz crystals were obtained. At 800° and higher tridymite was the only product. Inversion occurs therefore at about 800°, and the melting point of silica is really the melting point of tridymite, although by very rapid heating quartz can sometimes be melted without first changing into tridymite. Owing to the viscosity of the substance, it is exceedingly difficult to fix this point, but it seems probable that pure silica begins to melt at about 1600°.

To obtain a general idea of the behaviour of mixtures of lime and silica, small portions of finely-ground mixtures of known com-

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[1] Two crystals were measured.   [2] *Amer. J. Sci.*, 1906, [iv], **22**, 265.

position were placed in a row on platinum or iridium strip. The strip was gradually heated electrically and the order of melting noted. In this way two compounds and three eutectics were discovered. Mixtures containing more than 75 per cent. or less than $32\frac{1}{2}$ per cent. of lime could not be investigated, owing to the refractory nature of the oxides. The compounds formed are the metasilicate and the orthosilicate of calcium; the analogue, $4CaO,3SiO_2$, of åkermanite, and the tricalcic silicate, $3CaO,SiO_2$, could not be detected, although special efforts were made to prepare them.

The properties of the metasilicate have been already described. The orthosilicate, $2CaO,SiO_2$, melts at about 2080°, and exists in three polymorphic forms which stand in enantiotropic relation to one another. The α-form, which crystallises in the monoclinic system, is the only modification stable in contact with the fusion. Its specific gravity is about 3·27. Below 1410° the α-form changes into the β-form. This unstable modification is orthorhombic, and has about the same density as the α-form; it turns into the monoclinic γ-variety at about 675° with great increase of volume, the specific gravity of the latter being 2·974. The disintegration which takes place when the orthosilicate is cooled is thus explained. The orthosilicate is readily attacked by water, and this is probably the reason why it is not found as a mineral. The three eutectics are: tridymite and pseudo-wollastonite at 37 per cent. of lime, melting at 1417°; pseudo-wollastonite and α-orthosilicate at 54 per cent. of lime, melting at 1430°; α-orthosilicate and lime at $67\frac{1}{2}$ per cent. of lime, melting at 2015°.

The preliminary investigation having demonstrated the existence of two compounds and three eutectics, the melting points of 100 gram charges were determined by means of a thermo-junction, or for higher temperatures by the Holborn-Kurlbaum pyrometer. The results, which were plotted, fully confirmed the preliminary observations. It was found incidentally that pseudo-wollastonite appears to be capable of taking up small quantities of silica and of orthosilicate in solid solution.

The very important results obtained in the course of the investigation of the felspars and of the calcium silicates naturally led the workers in the geophysical laboratory at Washington to turn their attention to the compounds of magnesia and silica, and thanks to the labours of E. T. Allen, F. E. Wright, and J. K. Clement,[1] we now possess a very complete knowledge of the metasilicate, $MgSiO_3$. This substance can exist in four distinct crystal forms.

I. The first crystallises in the monoclinic system, and is the product usually obtained from fusions. It was first prepared by Ebelmen, and

[1] *Amer. J. Sci.*,[1906, [iv], **22**, 385.

is found in nature in certain meteorites. It can be made (1) by melting together magnesia and silica in the proper proportions and allowing the liquid to crystallise; (2) by allowing the glass obtained by rapidly cooling the fusion to crystallise at 1300°; (3) by heating any of the other forms to temperatures from 1150° upwards; (4) by fusing amorphous silica with magnesium tellurite or chloride; (5) by recrystallising magnesium silicate from a flux of magnesium chloride or vanadate, calcium vanadate or tellurium dioxide. The first method is most suited for preparing the substance in quantity; the last yields the best crystals, the most satisfactory results being obtained when the silicate is fused with magnesium chloride in a current of dry hydrogen chloride. The crystals resemble in some respects those of a monoclinic pyroxene, having the characteristic cleavage angle 92°, but the ratio $b : c = 0.77$ is very different from that of diopside $b : c = 0.5894$. They are characterised by the low extinction angle on b (010), $c : \mathfrak{r} = 21.8°$, and by polysynthetic twinning parallel to a (100). The specific gravity is 3·192 at 25°. The monoclinic pyroxene met with in the Bishopville meteorite has the same properties.

II. The second form is orthorhombic and identical with enstatite. It is best prepared by heating the glass to between 1000° and 1100°; if the latter temperature is exceeded the first variety appears as well, often in parallel intergrowths. Obtained in this way, the substance forms fibrous aggregates of specific gravity 3·175. The angle between the optic axes is smaller than that of natural enstatite, a fact as yet unexplained. On heating to temperatures above 1260° this form passes slowly into the monoclinic variety.

III. The third form is a monoclinic amphibole, and is the least clearly defined of the four. Its identification as a separate variety rests on its extinction angle, maximum value 11°, and on its mean refractive index, which is much lower than that of I. It is sometimes met with in fusions which have been rapidly cooled, and appears also to be produced by the action of water at 375—475° on the next variety.

IV. This form is orthorhombic, and is identified by the authors with a naturally occurring amphibole to which some writers have given the name of kupfferite. To prepare this variety the mixture should be heated well above the melting point and then cooled as quickly as is possible without forming glass. Measurable crystals have not been obtained, and the identification with kupfferite rests on the optical properties and the indication of cleavage at 120°. The mean specific gravity is 2·857 at 25°. This variety changes into I on heating. These four modifications stand in monotropic relation to one another, the order of increasing stability being orthorhombic amphibole, monoclinic amphibole, enstatite, monoclinic pyroxene,

That this is so is shown by the fact that enstatite and the amphiboles when heated pass over into the monoclinic pyroxene, which cannot be changed back without passing through the amorphous state. Further, it is found that although the first three forms can all be dissolved in suitable fluxes at comparatively low temperatures, yet they crystallise out as monoclinic pyroxene. Lastly, it has been shown by an ingenious application of Frankenheim's method that the first three forms change into the monoclinic variety with evolution of heat. The existence of a monotropic relation between the two great groups of amphiboles and pyroxenes is in accord with the work of other experimenters, and the formation of amphiboles in nature instead of pyroxenes may perhaps have been due to the viscosity of the magma from which they crystallised, while the presence in the Bishopville meteorite of intergrowths of pyroxene and enstatite suggests that it was rapidly cooled from a high temperature.

Certain meta- and ortho-silicates have also been studied from a somewhat different point of view by V. Pöschl,[1] who has prepared mixed crystals by melting the constituents together. Thus he finds that artificial diopside and hedenbergite from Elba mix in all proportions. The melting point curve corresponds to Roozeboom's type I, but is not quite regular and the specific gravities of the mixtures do not in all cases lie between those of the components. Experiments with enstatite and diopside indicate that these substances form an isodimorphous series, with a gap extending from $40CaMgSi_2O_6, 60Mg_2Si_2O_6$, to $50CaMgSi_2O_6$, $50Mg_2Si_2O_6$. The case is similar to that of the mixed sulphates of iron and magnesium, and the specific gravities are lower for the rhombic than for the monoclinic form. The melting point curve is of type V. Artificial mixtures of the isomorphous orthosilicates, Mg_2SiO_4 and Fe_2SiO_4, do not give a continuous series, the gap extending from $65Mg_2SiO_4, 35Fe_2SiO_4$ to $3Mg_2SiO_4, 97Fe_2SiO_4$. The melting point curve is of type I, but is not a straight line. Artificial mixtures of Mg_2SiO_4 and Ca_2SiO_4 give results indicating that these substances are isodimorphous.

The conditions under which quartz and tridymite crystallise from silicate fusions have also been studied by P. D. Quensel,[2] who has arrived at conclusions in the main much the same as those reached by Day and Shepherd. He found that when a mixture of 74 parts of oligoclase and 26 parts of amorphous silica was fused with small quantities of tungstic oxide, or in the presence of water supplied by driving a current of superheated steam through the fusion, small quartz crystals were formed. The effect of adding tungstic oxide was to lower the melting point and

[1] *Centr. Min.*, 1906, 571.

[2] *Centr. Min.*, 1906, 657, 728 ; see also a paper by Cosmo Johns, *Geol. Mag.*, 1906, 3, 118.

viscosity, and to increase the size and rapidity of formation of the crystals. On fusing silica with excess of sodium tungstate, tridymite was obtained, a fact previously noticed by Hautefeuille. As there seemed reason to think that the amount of "mineraliser" present (in this case tungstic oxide or sodium tungstate) had an important influence on the result, fresh experiments were undertaken in which the oligoclase-silica mixture or pure silica were fused with from one to five parts of sodium tungstate. It was found, however, that quartz was always obtained from the oligoclase-silica mixture at temperatures below 1000°, while if silica alone was used, tridymite or glass were formed, according as the temperature was kept above or below 1000°, the amount of sodium tungstate present being unimportant. Quensel therefore concludes that the factors which determine the products are, the presence of co-solutes, the concentration, and the existence of chemical equilibrium, and explains the formation of quartz as due to the influence of the constituents of oligoclase on the equilibrium between the alkalis and silicic acid. In the case of tridymite a sodium silicate or possibly a silicotungstate is perhaps first formed, and this being unstable at high temperatures the silica separates directly as tridymite. The rare occurrence of tridymite in eruptive rocks, in spite of the fact that the temperature conditions would favour its formation, he explains as due to the special conditions required to produce this form, the presence of other substances interfering with its crystallisation.

Quensel finds that the melting point of tridymite is about 1560°, and concludes from his own work and from that of his predecessors that above 900° it is the stable form of silica. It can, however, exist at temperatures as low as 300° to 400°. Quartz, on the other hand, can exist up to 1000°, but is unstable above 900°. Below 200° the hydroxides are perhaps to be considered the stable form, though quartz can exist as well.

While the Americans have been breaking fresh ground in the study of pure silicates, C. Doelter has been very active in the field he has made especially his own. Many pages of the numerous and lengthy papers for which he and his pupils are responsible are occupied by adverse criticism of the views held by Vogt and of the results obtained by Day and Allen, but a certain amount of fresh work along the lines already familiar has been accomplished. Thus Doelter [1] himself has redetermined the melting points of a number of natural felspars, and has obtained results lower than those given by Day and Allen in their work on the artificial compounds. Further, he has reiterated his belief that when silicates are melted they dissociate to a very considerable extent into oxides, and has laid great stress on the part played by viscosity,

[1] *Wien. Sitzungsber.*, 1906, **115**. 723; *Monatsh.*, 1906, **27**, 433; *Tsch. Min. Mitt.*, 1906, **25**, 79 and 206; *Zeit. Elektrochem.*, 1906, **12**, 413; *Centr. Min.*, 1906, 193.

In a succeeding paragraph the mixed crystals formed by Mg_2SiO_4 and Fe_2SiO_4 are shown to belong to type I of Roozeboom's classification, and the importance of zonal structure as indicating a slight degree of supersaturation is pointed out. Arguments are also adduced to show that the mixed crystals formed by enstatite and diopside fall under Roozeboom's type IV. The results obtained by Day and Allen are utilised in the elaborate discussion of the felspars which occupies the second half of Vogt's paper and is devoted mainly to the consideration of mixed crystals composed of orthoclase, albite, and anorthite.   It is shown that whereas the binary mixture, albite and anorthite, belong to type I, the mixtures of orthoclase with albite or anorthite belong to type V and form eutectics. The ternary mixture in which all three components are present is also discussed and illustrated by a diagram. Further, the work of Schreinemakers [1] is applied to the case in which the mixture of orthoclase and albite is present with some independent component such as quartz or olivine. Such a case must fall either under Schreinemakers' type d or type e, and it is stated that the combination quartz, orthoclase, albite belongs to the second of these, and yields as final product a ternary eutectic mixture of quartz and the two kinds of mixed crystals. A full discussion of some of the latter points is to be given in a continuation of the paper.

Deposition of Quartz from Aqueous Solutions.—J. G. Königsberger and W. J. Müller [2] have attempted to throw light on the conditions under which quartz and other vein minerals have been deposited, more especially in the case of those found in the biotite-protogine of the Aar.   Assuming that these minerals have crystallised from solutions having approximately the composition of the inclusions found in the quartz crystals of the district (see page 323) at temperatures between $120°$ and $500°$, they have attempted to imitate the conditions of their formation by heating glass and obsidian with water and carbon dioxide in a steel bomb lined with platinum-iridium.   The bomb was heated in an electrical oven in which it could be shaken and inverted. On inversion a filtering arrangement came into action which enabled them to examine separately the crystals deposited from the solution on cooling.

The composition of the glass (I) and obsidian (II) was :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.
I.	69·21	2·48	0·45	0·52	9·84	1·98	11·91	—
II.	74·3	13·0	2·6	0·3	1·00	4·6	3·8	0·3

The glass was completely decomposed on heating with water to $360°$, and quartz crystals and some opal were found to have separated from the solution.   The residue in the tube consisted chiefly of amorphous

[1] *Zeit. physikal. Chem.*, 1905, **51**, 569.
[2] *Centr. Min.*, 1906, 339, 353.

silica, together with tridymite and a little quartz. The glass was also decomposed if the water contained small quantities of carbon dioxide, but if much was present the glass was less readily attacked. Obsidian treated with water was more resistant than glass, but on adding sodium bicarbonate decomposition took place and quartz was formed. When heated to 420° with a solution of the composition of the quartz inclusions, obsidian was partially converted into a substance identified with aegirine-augite. Zeolites were not observed in these experiments. Quartz, muscovite, and adularia were all more or less attacked by water at 350°, and dissolved completely when heated to the same temperature with a 20 per cent. solution of sodium carbonate, carbon dioxide escaping from the tube, which was not quite tight. On the other hand, water containing both carbon dioxide and sodium carbonate had very little action on quartz, adularia, sphene, muscovite, biotite, calcite, or fluorite at 370°. The action of alkali carbonates first becomes considerable at those temperatures at which they are strongly hydrolysed. The addition of carbonic acid diminishes the hydrolysis, and in consequence the action of the alkali. This is in harmony with the experiments of Spezia, who found that the action of a solution of borax on quartz was diminished by the addition of boric acid. The most important conclusion arrived at by the authors is that in the system composed of silicic acid, alkalis, and a weak acid such as carbonic acid or boric acid in aqueous solution, the deposition of quartz can only be explained by a change in the equilibrium point of a reversible reaction, the acidity of the silicic acid increasing with greater rapidity as the temperature rises than it does in the case of the other weak acid present. They also point out that the simultaneous production of quartz, tridymite, opal, and chalcedony is in harmony with van't Hoff's rule that high valence favours the existence of labile compounds.

The Silicic Acids.—G. Tschermak [1] and his pupils have carried out a good deal of new work on the lines described last year, and believe that they have established the existence of several new silicic acids, and thereby thrown light on the constitution of a number of minerals. Ilvaite, anorthite, and olivine all yield metasilicic acid, H_2SiO_3, and must therefore be regarded as metasilicates. Willemite and monticellite are orthosilicates. Pectolite and wollastonite both yield $H_6Si_3O_9$, and wollastonite is therefore $Ca_3Si_3O_9$. Meerschaum from Asia Minor also gave an acid, $H_6Si_3O_9$. Massive and foliated serpentine and also chrysotile were found to have the composition $H_4Mg_3Si_2O_9$, but whilst the latter gave an acid, $H_{10}Si_4O_{13}$, the former

[1] *Wien. Sitzungsber.*, 1906, **115**, i, 217, 697 ; *Anzeiger K. Akad. Wiss. Wien.*, 1906, **19**, 339.

gave $H_8Si_4O_{12}$, and the same substance was obtained from the pseudomorphs of serpentine after olivine from Snarum. Chrysotile is therefore to be written $H_4(MgOH)_4(MgOMg)Si_4O_{18}$, and serpentine $H_2(MgOH)_6Si_4O_{12}$. From datolite and gadolinite a new pulverulent acid, $H_2Si_2O_5$, was obtained. Heulandite, taken to be $H_{12}CaAl_2Si_6O_{22}$, gave an acid, $H_{10}Si_6O_{17}$, and must be written $H_8(CaO_2Al_2O_3H_2)Si_6O_{17},H_2O$, the bivalent group HOAlOCaOAlOH being present. They find, moreover, that heulandite lost calcium when exposed to the action of a considerable quantity of water, and therefore conclude that it was probably deposited from a concentrated solution.

Constitution of Zeolites.—Reference was made last year[1] to the experiments of F. Zambonini on heulandite and on thomsonite, by which he attempted to throw light on the vexed question of the part played by water in these compounds. The conclusion to which he then came was that these minerals are comparable to the hydrogels described by van Bemmelen. He has been confirmed in this view by his recent researches,[2] which have been conducted on lines similar to those already described. Thus he finds that the dehydration of, and the reabsorption of water by, gelatinous silica prepared from potassium silicate follows much the same course as in the case of the zeolites. The amorphous nickel ore garnierite, $(Mg,Ni)SiO_3,nH_2O$, from Noumea, New Caledonia, on the other hand, exhibits a very different behaviour from heulandite and thomsonite as regards its capacity for reabsorbing water after partial dehydration at various temperatures. This substance is probably a solid solution, and it is therefore hardly likely that the zeolites are to be regarded as having the same constitution. Further, he concludes that the water taken up again by zeolites after they have been heated is more loosely held than the water originally present, and he bases this statement on the dehydration curves of the rehydrated zeolite. Lastly, observations made on dioptase lead him to the somewhat remarkable conclusion that in the case of this mineral we meet with example of solid solution.

The constitution of certain silicates has also been discussed by H. C. McNeil,[3] who, continuing the line of research begun on F. W. Clarke, has examined the behaviour of various mineral treated with strong solutions of hydrochloric acid and carbonate both before and after ignition. He finds that talc has been strongly heated contains one-fourth of its silica in a soluble in sodium carbonate, the residue being completely decom by hydrochloric acid. He concludes that talc contains both an and a tri-silicate radicle, and that the latter on ignition turns int Si_2O_5 group Pyrophyllite he regards as a true acid metasilic

[1] *Ann. Report*, 1905, 271.   [2] *Mem. R. Accad. Lincei*, 1906, **6**, 10
[3] *J. Amer. Chem. Soc.*, 1906, **28**, 590.

The results obtained with kaolin accord with the supposition that it is an orthosilicate, $HOAl(OSiO_3H_3)(OSiO_3Al)$, converted, on heating, into $Al_2Si_2O_7$ and water. Halloysite on ignition also gives $Al_2Si_2O_7$, and may be regarded as kaolin combined with one molecule of water. McNeil has also carried out some experiments on zeolites, on the lines of those made by Steiger, but instead of using sealed tubes he has fused the minerals with various chlorides in platinum crucibles. As the result of experiments in which chabazite, stilbite, and thomsonite were fused with sodium chloride, he believes that these silicates belong to the same class and have the following general formula :

$$R''[XR''\{Al(XAl)(XH_2 \cdot AlO_2H_2)\}]_2.$$
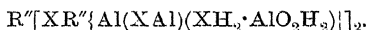
In thomsonite X is chiefly SiO_4 in stilbite Si_3O_8, and in chabazite a mixture of both these groups.

Mutual Relations of Fused Chlorides.—Some fresh light has been thrown on the minerals of the cerargyrite family by the work of K. Mönkemeyer,[1] who has studied the freezing point curves of binary mixtures of AgCl, AgBr, and AgI. These three substances melt at 452°, 422°, and 552° respectively. The two former crystallise in the holohedral class of the cubic system, but the iodide is dimorphous, the cubic form being stable above $146\frac{1}{2}°$, whilst below that temperature the substance forms hexagonal crystals. In the case of the mixture AgCl–AgBr, the freezing point curve is of type III of Roozeboom's classification. A continuous series of mixed crystals of the same kind is formed, and a minimum freezing point lying below the melting point of the more fusible constituent is reached. The minimum 412° was found to correspond to the mixture containing 35 per cent. of silver chloride. The mixtures of bromide and iodide also conform to type III, the minimum value of the freezing point being 377°, corresponding to the mixture containing 73 per cent. of silver bromide. In this case the phenomena are further complicated by the transformation of cubic into hexagonal crystals conditioned by the presence of the iodide. This transformation falls under type IA of Roozeboom's scheme, the mixed crystals forming a continuous series before and after the change, only one component being dimorphous. In the case of the chloride and iodide mixture the freezing point curve is of type V. The series of mixed crystals is interrupted, and a eutectic occurs containing 42 per cent. of silver chloride and solidifying at 211°. The chloride is only capable of taking up very small quantities of iodide, while the latter will mix with as much as 13 per cent. of chloride. The transformation into hexagonal crystals conforms to type IIIA. The view suggested by L. J. Spencer's study of iersite, that silver iodide

[1] *Jahrb. Min.* 1906, *Beil.-Bd.,* 22, 1.

is trimorphous, has not received any confirmation from these experiments.

Water of Crystallisation.—The difficult question as to the manner in which the elements of water are combined in minerals has been attacked by W. W. Coblentz[1] in an ingenious way. The infra-red absorption spectrum of water exhibits well-marked bands at the approximate wave-lengths 1·5, 2, 3, 4·75, and 6μ, those at 3 and at 6 being especially strong. Coblentz has therefore examined a large number of minerals to see if those containing so-called "water of crystallisation" show the water bands. In the case of selenite, $CaSO_4,2H_2O$, he found that these bands were strongly marked, with the exception of that at 4·75, the place of which was taken by a strong band at 4·55. Anhydrite, $CaSO_4$, on the other hand, did not show the water bands, although in this case also the band at 4·55 was prominent. This band was subsequently found to be well shown by anglesite, barytes, and celestine, as well as by glauberite, kieserite, and thenardite; it is doubtless due to the SO_4 ion. Opal, heulandite, stilbite, natrolite, and scolecite all showed the water bands. On examining hydroxides the water bands were found to be wanting, with the exception of that at 3, which appears to be characteristic of this class of substances. This was found to hold for manganite, göthite, bauxite, turquoise, lazulite, hydrargyllite, and diaspore. In the case of datolite and azurite the band at 3 was slightly displaced, while brucite exhibited a complex band with maxima at 2·5, 2·7, and 3. Tourmaline showed bands at 1·28 and 2·82. The examination of chloritoid, clinochlore, pennine, the micas, and talc revealed no indication of the presence of hydroxyl. On the other hand, this group probably exists in serpentine, which shows a well-marked band at 3μ.

New Minerals.

Bellite.—This mineral has been described by W. F. Petterd.[2] It occurs in delicate tufts and velvety coatings lining cavities in a soft iron-manganese-gossan at Magnet silver mine, Magnet, Tasmania. Minute hexagonal scales are sometimes met with. The colour is bright crimson to orange-yellow. Sp. gr. 5·5.

The following analysis is by J. D. Millen :

SiO_2.	PbO.	CrO_3.	SO_3.	As_2O_5.	P_2O_5.	V_2O_5.	Al_2O_3.	Cl.	Total.
7·59	61·68	22·61	0·05	6·55	0·04	0·11	0·01	0·52	99·16

Chlormanganokalite.—A preliminary account of this mineral has been given by H. J. Johnston-Lavis,[3] who found it in the form of canary-yellow rhombohedra associated with halite inside a block ejected

[1] *Physical Review,* 1906, **23**, 125.

[2] *Tasmania. Report of Secretary for Mines for* 1904. *Hobart,* 1905, 83.

[3] *Nature,* 1906, **74**, 103. See also A. Lacroix, *Compt. rend.,* 1906, **142**, 1249.

from Vesuvius. Analysis shows that the mineral is essentially a double chloride of manganese and potassium containing 38·97 per cent. of $MnCl_2,4H_2O$ and 57·71 per cent. of KCl.

Chlornatrokalite.—This name has been given by Johnston-Lavis [1] to a *sylvite* containing 12 per cent. of NaCl, found associated with chlormanganokalite.

Gorceixite is a barium aluminium phosphate. It occurs in brown pebbles, so-called "favas," in the diamond sands of Brazil, and has been described by E. Hussak.[2] Omitting silica (present as included quartz grains), ferric oxide, and TiO_2, the two following analyses by G. Florence lead to the formula $BaO,2Al_2O_3,P_2O_5,5H_2O$, a portion of the barium being replaced by calcium and cerium, and occasionally by strontium :

	SiO_2.	TiO_2.	BaO.	CaO.	CeO.	Al_2O_3.	Fe_2O_3.	P_2O_5.	H_2O.
I.	1·55	0·67	15·42	3·55	1·55	35·00	4·10	22·74	14·62
II.	6·5	0·75	15·30	2·24	2·35	35·20	1·67	21·47	14·73

Harttite.—E. Hussak [3] has assigned this name to a strontium aluminium sulphato-phosphate found in flesh-coloured "favas" in the diamond sands of Brazil. The mineral is related to svanbergite, $2SrO,3Al_2O_3,P_2O_5,2SO_3,6H_2O$, and has been analysed by G. Florence, with the following results :

TiO_2.	Al_2O_3.	SrO.	CaO.	CeO.	P_2O_5.	SO_3.	H_2O.
1·42	33·66	16·80	2·80	1·02	21·17	11·53	12·5:

These numbers lead to the formula $(Sr,Ca)O,2Al_2O_3,P_2O_5,SO_3,5H_2O$.

Hydrated Calcium Carbonate.—A deposit from the neighbourhood of Novo-Alexandria, looking much like mould or a thin layer of cotton-wool, has been examined by L. L. Ivanoff,[4] who finds that it consists of very thin, colourless, transparent, monoclinic or triclinic needles. When kept over calcium chloride at 22°, it loses 37·56 per cent. of water, leaving practically pure calcium carbonate behind. It is to be regarded as a hydrate, $CaCO_3,nH_2O$, where n is not less than 3.

Kertschenite.—At one or two localities in the Kertsch Peninsula there is found a dark green or almost black mineral. The formula $(Fe,Mn,Mg)O,Fe_2O_3,P_2O_5,7H_2O$ has been given to it by S. P. Popoff [5] on the ground of the two following analyses :

P_2O_5.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	H_2O.	Total.
28·19	32·89	9·50	1·99	1·51	0·49	25·04	99·64
28·21	32·965	9·49	1·84	1·56	0·46	24·91	99·435

New Mercury Mineral.—In 1903 A. J. Moses described two new mineral species, eglestonite and terlinguaite, both oxychlorides of mercury, from the Terlingua district, Texas, and indicated the probable existence of a third. The last is now under investigation by W. F.

[1] *Nature*, 1906, **74**, 174.　　　　[2] *Tsch. Min. Mitt.*, 1906, **25**, 335.
[3] *Ibid.*, 335.　　　　[4] *Ann. Geol. Min. Russie*, 1905, **8**, 23.
　　　　　　　　　　[5] *Centr. Min.*, 1906, 112.

Hillebrand and W. T. Schaller.[1] The preliminary examination has rendered it almost certain that this remarkable substance is a mercur-ammonium salt. It has so far been shown to contain Hg,N,Cl,SO_4, probably O, and possibly H. Further, P. G. Nutting has found that it gives off a little helium on warming. The full account of this as yet unnamed mineral will be awaited with interest. In the mean-time we may note that A. Sachs[2] has suggested that the oxychloride of mercury, $3HgO,HgCl_2$, described by him last year under the name of kleinite, may be identical with the substance referred to by Hille-brand. He finds, in fact, that both the sulphur-yellow and the orange-red varieties of kleinite yield small and variable amounts of SO_4 and ammonia, and he suggests that a portion of the chlorine in the above formula is perhaps replaced by SO_4, whilst oxygen is substituted by NH_2. If these views are accepted, the formula of kleinite becomes $Hg_4[Cl,\frac{1}{2}SO_4]_2[O(NH_2)_2]_3$.

Moravite.—Under this name F. Kretschmer[3] has described a new member of the leptochlorite family, found in considerable quantity in the neighbourhood of Gobitschau, near Sternberg, Moravia. It occurs in scales and lamellæ, iron-black in colour, and in physical characters and mode of occurrence it somewhat resembles thuringite, from which it may be distinguished by its superior hardness and lower specific gravity, as well as by its different composition. The results obtained on analysis of two different carefully selected specimens were as follows :

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O+Na_2O.	P_2O_5.	C.	H_2O.
I.	49·30	22·71	5·04	13·99	trace	1·82	1·10	trace	0·55	4·95
II.	50·69	19·62	10·42	8·30	0·84	1·46	(?)	0·93	(?)	5·02

From I is derived the formula $H_4(Al,Fe)_4(Fe,Mg)_2Si_7O_{24}$. The other members of the group found at Gobitschau are :

Thuringite, $H_{18}(Al,Fe)_8(Fe,Mg)_8Si_6O_{41}$.

Stilpnochlorane, $H_{24}(Al,Fe)_{10}(Ca,Mg)Si_9O_{46}$.

Stilpnomelane, $H_{12}(Al,Fe)_2(Fe,Mg)_8Si_{10}O_{37}$.

Nepouite.—Under this name E. Glasser[4] has recently described a mineral somewhat resembling Breithaupt's connarite. It occurs in the form of a crystalline powder at Népoui, New Caledonia. Five different specimens have been analysed, and the results quoted below are in harmony with the formula $2SiO_2,3(Ni,Mg)O,2H_2O$, nickel and magnesium being mutually replaceable in all proportions :

	SiO_2.	NiO.	MgO.	FeO.	CaO.	Al_2O_3.	H_2O.	Total.	Sp. gr.
I.	32·84	49·05	3·64	1·90	0·50	0·97	9·64	98·54	3·24
II.	33·08	46·11	6·47	2·20	traces	1·39	10·61	99·81	3·18
III.	35·05	39·99	11·80	1·22	0·58	1·13	10·05	99·82	2·89
IV.	40·07	18·21	29·84	0·25	0·53	0·72	11·98	101·60	2·47
V.	32·36	50·70	3·00	0·62	traces	0·69	12·31	99·68	3·20

[1] *Amer. J. Sci.*, 1906, [iv], **21**, 85.   [2] *Centr. Min.*, 1906, 200.
[3] *Ibid.*, 293.   [4] *Compt. rend.*, 1906, **143**, 1173.

Oehrnite.—The formula $6SiO_2,6(Mg+Fe,Ca)O,H_2O$ has been given by E. S. Fedoroff[1] to a mineral of the following composition:

SiO₂.	Al₂O₃.	Fe₂O₃.	FeO.	MgO.	CaO.	Na₂O.	K₂O.	H₂O.
49·47	6·74	0·28	6·33	16·80	17·74	0·38	0·18	2·41

It occurs in the Jenashir district of the Caucasus and somewhat resembles diallage in appearance. It has three rectangular cleavages, (100), (010), (001), the latter being highly perfect, but crystallises in the monoclinic system as shown by the optical characters. The optic axes lie in the plane of symmetry, the acute positive bisectrix making an angle of 55° with the normal to (001). The angle $2V$ is 63.

Osannite is a variety of amphibole, intermediate between riebeckite and arfvedsonite, and is found in the gneissic rocks of Cevadaes, Portugal. The optical characters have been determined by C. Hlawatsch,[2] who points out that in the amphiboles these properties vary with the ratio $Al_2O_3 : Fe_2O_3$, and also possibly with the amount of water present. The following analysis is due to M. Dittrich:

SiO₂.	TiO₂.	Al₂O₃.	Fe₂O₃.	FeO.	MnO.	MgO.	CaO.	Na₂O.	K₂O.	H₂O.	Total.
49·55	0·34	0·97	16·52	20·38	1·30	0·16	0·90	6·53	0·85	1·85	99·35

Otavite is a basic cadmium carbonate containing 61·5 per cent. of cadmium, found by O. Schneider[3] as white to reddish crusts lining cavities on two specimens from the Tschumeb mine, Otavi, German South-West Africa. The crusts consist of minute rhombohedra ($rr' = 80°$ about), which dissolve with effervescence in hydrochloric acid, and exhibit a metallic to adamantine lustre.

Paratacamite.—G. F. Herbert Smith[4] has proposed this name for a mineral of the same composition as atacamite, $CuCl_2,3Cu(OH)_2$, which he has observed on some specimens from Chili. The crystals are of two habits, namely, rhombohedral and prismatic. They are frequently twinned, and have a good cleavage parallel to the rhombohedron faces. The specific gravity is 3·74. The refractive index, 1·846. On heating the mineral it appears to give up its water rather more readily than does atacamite. According to G. T. Prior, the composition is:

CuO.	Cu.	Cl.	H₂O.
56·10	14·27	15·97	14·10

Paravivianite.—Radiating needle-like crystals, transparent and somewhat blue in colour, occur in the limonite ore of the Kertsch Peninsula. The formula $(Fe,Mn,Mg)_3P_2O_8,8H_2O$ has been found by

[1] *Gorni Journal*, 1905, 264.
[2] *Festschrift Harry Rosenbusch, Stuttgart*, 1906, 68.
[3] *Centr. Min.*, 1906, 389.   [4] *Min. Mag.*, 1906, 14, 170.

S. P. Popoff [1] to agree well with the analytical results.   No ferric iron is present.

P_2O_5.	FeO.	MnO.	MgO.	CaO.	H_2O.	Sp. gr.
27·01	39·12	2·01	1·92	0·48	29·41	2·66

Patronite.—Under this name F. Hewett [2] has recently described a dark green substance containing vanadium, which appears to occur in some quantity at Cerro de Pasco, Peru.   A specimen of the crude ore was found to contain 16 per cent. of vanadium and 54 per cent. of sulphur, with considerable quantities of silica, alumina, and iron.   It is at present undergoing examination at the hands of Dr. Hillebrand.

Rutherfordine.—This interesting mineral occurs associated with mica in German East Africa, and is an alteration product of pitch-blende.   The following analysis by W. Marckwald [3] shows that it is uranyl carbonate, UO_2,CO_3.   In appearance it resembles uranochre.

UO_3.	CO_2.	PbO.	FeO.	CaO.	H_2O.	Gangue.	Total.	Sp. gr.
83·8	12·1	1·0	0·8	1·1	0·7	0·8	100·3	4·82

Silicomagnesiofluorite.—This curious · mineral has been found as a loose block composed of radiating hemispherical aggregates, grey or green in colour, at Luppiko, in the neighbourhood of Pitkäranta, Finland.   It has been examined by P. A. Zemjatschensky,[4] who assigns to it the formula $H_2Ca_4Mg_3Si_2O_7F_{10}$, which he thinks may also be written in the form $Mg(OH)F,MgSiO_3,Ca(OH)F,CaSiO_3F_2,2CaF_2,MgF_2$, The fibres show straight extinction and weak positive double refraction.   The specific gravity is 2·9125 at 20°.

Weinbergerite.—In the course of an examination of the Kodaikanal meteorite, F. Berwerth [5] has found a new silicate in the form of spherules exhibiting fibrous structure, associated with diopside, bronzite, apatite, and chromite.   It appears to crystallise in the orthorhombic system, and its refraction and double refraction are both very low.   There is reason to believe that it is pseudomorphous. According to E. Ludwig, the composition is :

SiO_2.	TiO_2.	P_2O_5.	Fe_2O_3.	Al_2O_3.	Cr_2O_3.	MnO.	CaO.	MgO.
42·0	0·70	0·88	28·75	9·42	0·98	trace	3·87	4·47

K_2O.	Na_2O.	H_2O.	Total.
2·57	3·19	2·17	99·0

If we assume that the iron was present as FeO, that the water is not essential, and that P_2O_5 and Cr_2O_3 are due to the presence of apatite and chromite respectively, it will be found that the composition can be represented by the formula $NaAlSiO_4 + 3FeSiO_3$, some of the

[1] *Centr. Min.*, 1906, 112.   [2] *Engin. Mining Jour.*, 1906, **82**, 385.
[3] *Centr. Min.*, 1906, 761.   *Zeit. Kryst. Min.*, 1906, **42**, 209.
[5] *Tsch. Min. Mitt.*, 1906, **25**, 179.

sodium being replaced by potassium, and some of the iron by magnesium and calcium.

Yttrocalcite.—A mineral described under this name by E. S. Fedoroff [1] in 1905 has proved on further investigation to be identical with fluorapatite. [2]

Yttrocrasite.—This name has been assigned by W. E. Hidden and C. H. Warren [3] to an yttrium-thorium-uranium titanite. The material for analysis was derived from a single crystal weighing some sixty grams, found about three years ago in Burnet County, Texas, where the mineral occurs in loose pegmatite. The crystal exhibited orthorhombic symmetry and resembled certain yttrotantalites.

It was covered with a thin brown coating, the underlying material being black with pitchy lustre. Optical examination of thin slices showed that it was not strictly homogeneous, but consisted of istropic and of feebly doubly refracting portions. Sp. gr. 4·8043 at 17°. The following are the results of Warren's analysis:

TiO_2.	WO_3.	UO_3.	CO_2.	$(Yt,Er)_4O_3$.	Ce_2O_3, &c.	Fe_2O_3.	ThO_2.	UO_2.
49·72	1·87	0·64	0·68	25·67	2·92	1·44	8·75	1·98

		PbO.	MnO.	CaO.	H_2O.	Total.
		0·48	0·13	1·83	4·46	100·57

A small quantity of Cb_2O_5 together with traces of Ta_2O_5, SiO_2, and MgO, were also found, and of the water 0·10 per cent. was hygroscopic. These numbers give the following approximate molecular ratios: $H_2O : R''O : R'''_2O_3 : R''''O_2 : TiO_2 = 6 : 1 : 3 : 1 : 16$, where $R''O$ is chiefly lime, R''_2O_3 chiefly yttrium earths, and $R''''O_2$ chiefly thoria. The mineral is therefore essentially a hydrous titanate of the yttrium earths and thorium, but the fact that it contains both water and carbon dioxide, taken in conjunction with the results of the microscopic examination, suggests that it may be a hydrated alteration product of an originally anhydrous species. The radioactivity of the substance has been determined by B. B. Boltwood, who finds that it corresponds to 10 per cent. of thorium and 2·08 per cent. of uranium.

A New Zeolite.—A. Pauly [4] has examined the minute grains scattered through a quartz-sericite rock which occurs in the neighbourhood of Hainburg. He finds that they are isotropic and possess a good cleavage parallel to faces of the cube. The index of refraction is 1·507—1·508 for sodium light, and is therefore higher than that of analcime. Microchemical tests showed the presence of Na, Ca, Si, Al, and SO_4. About 10 per cent. of water was driven off on heating, proving that the mineral is not a member of the sodalite group. The specific gravity is 2·4—2·5. The author has been unable so far to obtain

[1] *Gorni Journal*, 1905, 264. [2] *Private communication* from E. S. Fedoroff.
[3] *Amer. J. Sci.*, 1906, [iv], **22**, 515. [4] *Zeit. Kryst. Min.*, 1906, **42**, 370.

sufficient material for a quantitative analysis, but thinks that his results justify him in concluding that the mineral is new.

Artificial Formation of Minerals.

A number of cases of the artificial production of minerals have been mentioned incidentally in a previous section, but a few special experiments deserve a separate description here.

Diamond.—A useful summary of the attempts that have been made to obtain this form of carbon has been contributed by A. Koenig[1] to the pages of the *Zeitschrift für Elektrochemie.*

Forsterite.—Allen and Wright[2] obtained Mg_2SiO_4 as a by-product when $MgSiO_3$ was dissolved in fluxes and allowed to crystallise. The best specimens were furnished by magnesium chloride. The crystals were small, but gave fairly sharp measurements, and agreed in habit, angles, and physical characters with the natural mineral. *Periclase* was also observed in some of these experiments in well-formed octahedra.

Nordenskiöldite.—Minute but measurable rhombohedra of this substance, CaO,SnO_2,B_2O_3, have been obtained by L. Ouvrard[3] by passing a mixture of air and stannic chloride vapour over calcium borate at a bright red heat.

Northupite, $2MgCO_3,2Na_2CO_3,2NaCl$, is probably isomorphous with tychite, $2MgCO_3,2Na_2CO_3,Na_2SO_4$, described by Penfield and Jamieson last year. To throw light on this point, A. de Schulten[4] has attempted to prepare mixed crystals of the two substances. In this he has been successful, for by heating mixtures of the chloride and sulphate of sodium in various proportions with 20 grams Na_2CO_3 and 18 grams $Mg_2SO_4,7H_2O$, dissolved in 350° c.c. of water, he has obtained crystals containing 99, 76, 64, 28, and 6 per cent. of tychite respectively. He concludes, therefore, that the two substances are perfectly isomorphous.

Quartz has been produced in measurable crystals by Day and Shepherd[5] by heating a mixture of ammonium magnesium chloride, sodium metasilicate, and water for three days in a steel bomb at 400—450°. The clear, colourless crystals attained a maximum length of 2 mm. They were doubly terminated and often barrel-shaped, showing rhombohedron faces passing by oscillatory developments into steeper rhombohedra, and finally into the prisms which showed the characteristic striæ. In some the + rhombohedron only was present. The angle from prism to rhombohedron was 37°48′ instead of

[1] *Zeit. Elektrochem.*, 1906, **12**, 441.   [2] *Amer. J. Sci.*, 1906, [iv], **22**, 390.

[3] *Compt. rend.*, 1906, **143**, 315.   [4] *Ibid.*, 403.

[5] *Amer. J. Sci.*, 1906, [iv], **22**, 297.

38°13′, this being perhaps due to some ingredient of the mixture held in solid solution.

Some interesting experiments on the crystallisation of quartz have also been carried out by G. Spezia.[1] He suspended a long crystal and three short prisms of quartz cut perpendicular to the axis in the lower portion of a tube containing a 2 per cent. solution of sodium metasilicate which was kept at a temperature of about 330° at the upper end, whilst the lower end remained at about 170°. The upper part of the solution was in contact with a quantity of powdered quartz. After heating for one hundred days, it was found that a quantity of silica had dissolved and had been deposited again on the prisms, converting them into more or less perfect crystals. The long crystal had also increased in size. It was observed that quick crystallisation appeared to favour the development of a long prism terminated by the faces of one rhombohedron. Slow crystallisation, on the other hand, gave a short prism terminated by the faces of two rhombohedra.

Mineral Analyses.

Many mineral analyses have been published during the past year. It is only possible here to refer very briefly to some of those which have thrown light on the composition of rare or imperfectly described species, or which are of special importance, because made on carefully selected material of which the crystallographic and physical characters have also been determined. For the rest, reference should be made to the Abstracts published by this Society.

Apatite.—Crystals from the Rhone glacier have been the subject of an elaborate crystallographic and optical study by K. Busz.[2] He finds $a : c = 1 : 0.7335$, and that for sodium light, $\omega = 1.63558$, $\epsilon = 1.63320$. A second prism gave slightly different values. The analysis quoted below shows that the substance is a pure fluor-apatite.

P_2O_5.	Al_2O_3.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	F.	Sp. gr.
41·44	0·94	0·39	54·80	0·14	0·45	0·53	0·22	2·93	·3·195

Traces of iron and chlorine were found.

Apophyllite.—In a preliminary communication F. Cornu[3] announces that the extreme members of the leucocyclite type of apophyllite are free from fluorine, but contain hydroxyl; the specimens of the chromocyclite type, on the other hand, contain fluorine. The former are optically positive and possess higher indices of refraction than the latter, which are negative.

Berthierite.—This mineral occurs in some quantity at Charbes, Val

[1] *Atti R. Accad. Sci. Torino*, 1906, 41, 158.   [2] *Centr. Min.*, 1906, 753.
[3] *Ibid.*, 79.

de Villé (Weilerthal), Alsace. A specimen analysed by Ungemach[1]
gave the following results :

S.	Sb.	Fe.	As.	SiO_2.	Total.	Sp. gr.
28·02	54·06	12·72	traces	5·29	100·09	4·21–4·23

On subtracting the silica, numbers are obtained which agree well
with the formula FeS,Sb_2S_3.

Boleite Group.—G. Friedel[2] has published a comprehensive account
of this group, based on an examination of specimens preserved at the
École des Mines de Saint-Étienne, supplemented by some from the
École des Mines de Paris. He has also been able to study Mallard's
microscopic sections and some of Lacroix's preparations. He recog-
nises three distinct species in the group, namely, cumengeite, pseudo-
boléite, and boléite. All three crystallise in the tetragonal system,
and their chief properties are summarised below :

Name.	Formula.	Parameter c.	Sp. gr.	Birefringence.
Cumengeite	$4PbCl_2,4CuO,5H_2O$............	1·625	4·67	0·100
Pseudo-boleite ...	$5PbCl_2,4CuO,6H_2O$............	2·023	4·85	0·032
Boleite	$9PbCl_2,8CuO,3AgCl,9H_2O$...	3·996	5·054	0·020

The above formulæ differ considerably from those hitherto assigned
to members of the group, and are based on the following analyses, of
which I refers to cumengeite, II to pseudo-boleite, III gives the com-
position of pseudo-boleite on the assumption that the silver chloride pre-
sent is due to admixture with boleite ; IV is the mean of two concordant
analyses of boleite made, one on material derived from the exterior
of the crystals, the other on material from the interior. Under Ia,
IIIa, and IVa are given the theoretical percentages corresponding with
the formulæ. As the analysis of pseudo-boleite was made on 0·0948
gram only, and as the water yielded by this substance could only be
obtained by calculation from an estimation made on a mixture of
boleite and pseudo-boleite, of which the composition was but
approximately known, the formula assigned can only be regarded as
provisional.

	I.	Ia.	II.	III.	IIIa.	IV.	IVa.
Pb	54·47	54·46	53·5 ⎫	77·5	76·52	49·34 ⎧	49·93
Cl	19·03	18·68	20·2 ⎭			17·16	17·13
CuO	20·27	20·93	16 5	16·9	17·51	17·18	17·05
H_2O	5·90	5·93	[5·5]	5·5	5·97	4·35	4·35
Residue.......	0·19	—	0·8	—	—	0·23	—
AgCl	—	—	1·6	—	—	11·59	11·54

Breunnerite.—Large rhombohedra have been observed by G. Piolti[3]
in serpentine near Avigliana. The mean value of the rhombohedron
angle is 72°29′42″, whence $c = 0·808642$. The ordinary index of re-

[1] *Bull. Soc. franç. Min.*, 1906, **29**, 266.   [2] *Ibid.*, 14.
[3] *Atti R. Accad. Sci. Torino*, 1906, **41**, 1066.

fraction determined by the Duc de Chaulnes's method is 1·715. The composition is 90·47 per cent. $MgCO_3$ and 9·45 per cent. $FeCO_3$. Traces of manganese are present, but no calcium. A specimen from the Sylvester mine, Val de Villé, analysed] by Ungemach,[1] contained 3·10 per cent. $CaCO_3$, 35·08 $MgCO_3$, 61·25 $FeCO_3$, whilst another specimen from the same mine contained 52·65 per cent. $CaCO_3$, 25·47 per cent. $MgCO_3$, and 21·85 per cent. $FeCO_3$, and is therefore *ankerite*.

Two specimens from Frigido, near Massa, analysed by E. Manasse,[2] contained respectively 46·30 and 55·09 per cent. of FeO with 12·18 and 5·94 per cent. MgO. The former corresponds to $2FeCO_3,MgCO_3$, the latter to $5FeCO_3,MgCO_3$.

Two other specimens from Bottino, Tuscany, examined by the same analyst,[3] had a composition agreeing with the formula $3FeCO_3,MgCO_3$.

Calvrerite.—A measurable crystal found on a specimen from Laurium has enabled A. Sachs[4] to determine the constants of this mineral. He finds that it is monoclinic, $a:b:c = 0·82386 : 1 : 0·77672$; $\beta = 106°29'$. The composition of the apple-green crystals is as follows :

As_2O_5.	NiO.	CoO.	FeO.	MgO.	H_2O.	Total.	Sp. gr.
40·45	26·97	trace	1·10	6·16	25·26	99·94	3 0104

The mineral is isomorphous with erythrite, though the similarity of angle is not very close.

Calcite.—In the course of an interesting investigation into the cause of the persistent phosphorescence exhibited by certain specimens of calcite from Fort Collins, Colorado, and from Joplin, Missouri, W. P. Headden[5] has made a very careful analysis of the well-known yellow crystals from the latter locality. The results are as follows :

SiO_2.		CaO.	MgO.	MnO.	FeO.	ZnO.	
0·032	43·950	55·740	0·113	0·015	0·016	0·014	0·007

$(Di,Sm,La)_2O_3$.	$(Yt,Er)_2O_3$.
0·012	0·012

Traces of $SO_3, P_2O_5, Cl, SrO, Al_2O_3, Cr_2O_3, NH_3$ and Na_2O were observed, but no hydrogen sulphide could be detected, and of the gas evolved on dissolving 100 grams of material, all but 10 c.c. was absorbed by caustic potash. The author is inclined to attribute the remarkable phosphorescence to the presence of some member of the yttrium group. Specimens of other colours are found with the yellow ones, and those of

[1] *Bull. Soc. franç. Min.*, 1906, 29, 279.
[2] *Mem. Soc. Tosc. Sci. Nat.*, 1906, 22, 81.
[3] *Proc. verb. Soc. Tosc. Sci. Nat.*, 1906, 15, 20.   [4] *Centr. Min.*, 1906, 198.
[5] *Amer. J. Sci.*, 1906, [iv], 21, 301.

purple tint exhibit the absorption bands characteristic of didymia, but none of them shows the persistent phosphorescence.

Celestine.—A dolomite containing considerable quantities of celestine is found at the Woolmith quarry, near Maybee, Monroe County Michigan. Fine crystals of the mineral are met with in cavities in the rock, and have been the subject of crystallographic and chemical examination by E. H. Kraus and W. F. Hunt.[1] Axial ratio $a : b : c = 0·7781 : 1 : 1·2673$. Sp. gr. 3·979 at 20·5°. Analysis of clear, transparent crystals gave the following result:

SO_3.	S_1O.	BaO.	MgO.	CaO.	$(Al,Fe)_2O_3$.	SiO_2.	Total.
43·58	53·75	1·26	0·12	0·45	0·15	0·22	99·53
43·60	53·78	1·32	0·14	0·47	0·13	0·23	99·67

Chalmersite.—E. Hussak,[2] having received a fresh supply of this mineral from the St. John del Rey mine, has been able to place 0·0896 gram of pure material in the hands of G. Florence for a new analysis, the first having been made on 0·016 gram only. The results quoted below lead to the formula $CuFe_2S_3$ or Cu_2S,Fe_4S_5.

Fe.	Cu.	S.	Total.
43·13	22·27	35·11	100·51

Clintonite and Chlorite Group.—E. Manasse[3] has analysed a *chloritoid* (I) from Strettoia, Alpi Apuane, two specimens of *ripidolite*, from Calci (II) and Verruca (III) respectively, and a *clinochlore* from Affaccata (IV). The results are given below:

	SiO_2.	TiO_2.	Al_2O_3.		FeO.	MgO.	Na_2O.	H_2O.
I.	25·70	0.59	36·95		23·44	6·12		6·31
II.	26·14		28·65		18·38	19·48	0·56	11·93
III.	24·93		21·80		28·08	12·82	trace	11·64
IV.	28.95		21·41	3·12		34·07		12·86

In analysis I water was determined by ignition loss, and the iron all calculated as FeO, although Fe_2O_3 was also present.

Datolite.—A valuable contribution to our knowledge of this mineral has been made by E. H. Kraus and C. W. Cook,[4] who have examined the excellent crystals found at Westfield, Massachusetts. These crystals are rich in faces, and exhibit monoclinic symmetry with the following constants, $a : b : c = 0·63482 : 1 : 1·26567$; $\beta = 90°9'$. Careful determinations of the specific gravities of four crystals gave a mean value of 3·0058 at 21·5°. This composition is accurately expressed by the accepted formula $HCaBSiO_5$. Analyses II and III below were made on material derived from a single crystal. Under I is given the theoretical composition. Crystals of this mineral found at the

[1] *Amer. J. Sci.*, 1906, [iv], **21**, 237.   [2] *Centr. Min.*, 1906, 332.

[3] *Proc. verb. Soc. Tosc. Sci. Nat.*, 1906, **15**, 20.

[4] *Amer. J. Sci.*, 1906, [iv], **22**, 21.

Colebrook mine, Dundas, Tasmania, have been measured by C. Anderson,[1] who finds that they have the composition given under IV.

	SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	B_2O_3.	H_2O.	Total.
I.	37·63	—	—	34·95	—	21·81	5·61	—
II.	37·60	0·10	0·14	34·64	0·32	21·76	5·67	100·23
III.	37·58	0·10	0·16	34·74	0·31	21·94	5·76	100·59
IV.	36·28	0·95		35·21	—	20·48	6·48	99·40

Dundasite occurs in white spherical aggregates or in tufts of radiating silky needles associated with allophane and cerussite at Welsh Foxdale Mine, Trefriw, Carnarvonshire. G. T. Prior [2] finds that the analytical results suggest the formula, $PbO,Al_2O_3,2CO_2,4H_2O$:

PbO.	Al_2O_3.	Fe_2O_3.	CO_2.	H_2O>100°.	H_2O at 100°.	Insol.	Total.	Sp. gr.
43·20	21·39	1·61	16·45	13·60	1·41	1·80	99·46	3·25

-The Welsh mineral is like that from Tasmania, and shows a relation to dawsonite, $Na_2O,Al_2O_3,2CO_2,2H_2O$.

Fluorite.—In the course of an elaborate study of fluorescence, H. W. Morse [3] has examined the composition of the gases given off when fluorite is heated. In the case of specimens from Weardale these consisted chiefly of carbon monoxide, carbon dioxide, hydrogen, and nitrogen, with small quantities of oxygen. The two latter were not present in the proportions in which they occur in air, and no argon or helium was found. He concludes that the gases are due to the decomposition of some organic colouring matter, but that there is nothing to show that organic substances have anything to do with the fluorescence or thermo-luminescence of the mineral.

Garnet.—The chemical composition and optical constants of a number of garnets have been determined by M. Seebach.[4] His results are tabulated below :

    I. Grossular from Xalostoc, Mexico. Pink dodecahedra.

    II. Pyrope from Colorado River, Arizona. Blood-red masses.

    III. Pyrope from Meronitz, Bohemia. Dark, wine-red grains.

    IV. Almandine from Ceylon. Brown-red to wine-red grains.

    V. Almandine from Jeypoor. Irregular, dark-red fragments.

    VI. Melanite from Frascati. Well-developed, black crystals.

    VII. Andradite from Dognaczka. Green crystals.

VIII. Demantoid from Polewskoi-Zawod, Urals. Rolled masses.

	SiO_2.	TiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Total.
I.	40·79	—	21·70	—	0·18	0·43	1·07	35·63	0·39	100·19
II.	43·37	—	20·99	2·36	—	10·21	0·52	4·54	18·42	100·41
III.	42·98	—	21·34	2·06	0·95	7·80	0·50	4·47	20·67	100·77
IV.	37·25	—	19·43	—	3·29	35·15	1·24	2·51	1·13	100·30
V.	38·07	—	19·63	—	2·16	31·58	1·36	5·03	2·77	100·60
VI.	34·74	1·54	5·44	—	21·95	1·99	0·65	32·58	1·48	100·37
VII.	36·79	—	1·39	—	29·30	0·69	0·26	31·40	0·77	100·60
VIII.	35·37	—	1·54	1·32	28·89	0·52	0·34	32·26	0·21	100·45

[1] *Rec. Australian Mus.*, 1906, **6**, 133.   [2] *Min. Mag.*, 1906, **14**, 167.

[3] *Proc. Amer. Acad.*, 1906, 587.   *Inaug. Diss. Heidelberg*, 1906.

All the above are the mean of two concordant analyses, with the exception of VI, which is the mean of four analyses. The minerals were decomposed by fusion with anhydrous boric acid, and the analyses conducted by the methods developed by Jannasch and his pupils.

In the following table are given the specific gravities and optical constants of the minerals before fusion, the specific gravities and indices of refraction for sodium light (so far as the latter could be determined) after fusion, and the proportion of the fused mineral soluble in hydrochloric acid. The molecular ratios calculated from analyses III, V, and VII agree fairly well with those required by the garnet formula $R''_3R'''_2Si_3O_{12}$, but diverge considerably from the theoretical values in the case of analyses IV, VI, and VIII.

		Before fusion.			After fusion.		Percentage soluble in HCl.
No.	Sp. gr.	μLi.	μNa.	μTl.	Sp. gr.	μNa.	
I.	3·506	1·7319	1·7364	1·7411	2·866	1·6205	all
II.	3·715	1·7371	1·7417	1·7463	3·190	—	82
III.	3·679	1·7417	1·7463	1·7505	3·251	—	84
IV.	4·040	1·7724	1·7779	1·7825	3·009	—	72
V.	4·025	1·7763	1·7815	1·7862	·3·240	—	74
VI.	·3·774	1·8471	1·8560	1·8658	3·263	1·7667	97
VII.	3·660	1·8763	1·8878	1·8990	3·171	1·8177	all
VIII.	3·801	1·8767	1·8884	1·8999	3·335	1·8110	99

A few other analyses of garnet may also be recorded here. Of these I refers to a bright red *spessartite* from Kārarfvet near Falun, analysed by C. Benedicks[1]; II gives the composition of a brown variety from the same locality; these garnets are interesting because they contain an appreciable quantity of yttria; III is a dark brown garnet found in pegmatite at Yamanō, Hitachi Province, Japan; IV occurs in brown-red crystals in mica andesite at Anamushi, Yamato Province. The analyses were made by Shimizu.[2]

	SiO_2.	Al_2O_3.	Yt_2O_3.	FeO.	MnO.	CaO.	MgO.	Total.	Sp. gr.
I.	35·67	22·50	1·19	19·17	21·91	traces	—	100·44	4·197
II.	35·36	22·34	1·23	22·01	18·80	traces	—	99·74	4·068
III.	36·39	28·05	—	24·77	14·21	1·57	0·67	100·66	—
IV.	36·74	20·71	—	34·91	1·67	2·11	3·27	99·41	—

Geikielite.—A number of specimens of ferro-magnesian titanates from Ceylon, including the original geikielite (analysis I below), have been examined by T. Crook and B. M. Jones.[3] They find that this mineral contains a greater percentage of iron than was at first recorded, and they suggest that the formula should be written $(Mg,Fe)TiO_3$. The analyses II to X indicate a passage to picroilmenite, the composition of the latter being given under XI and XII.

[1] *Bull. Geol. Inst. Univ. Upsala*, 1906 (for 1901–5), **7**, 271.

[2] *Beiträge z. Min. Japan*, 1906, No. **2**, 53.   [3] *Min. Mag.*, 1906, **14**, 160.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
TiO₂ ..	63·77	64·41	64 78	60·02	60·87	61·60	62·25	63·94	64·03	62·49	57·64	56 08
FeO	6·34	5·44	5 92	5·51	6·03	7·79	11·58	10 09	12·14	10·70	16·57	24·40
Fe₂O₃..	1·93	2·77	2·22	6·80	5·69	4·95	—	0·25	—	3·54	10·17	5·43
MgO ...	28·50	27·90	27·90	27·79	27·29	26·81	26·03	25·79	24·66	23·60	15 56	14·18
	100·54	100 52	100·82	100 42	99·88	100·65	99·86	100 07	100·83	100·83	99·94	100·09
Sp.·gr.	—	3·97	3·89	3 79	3·87	3·90	3·91	4 01	4·11	4·01	4·17	4·25

Glaserite.—It has been maintained on the one hand that a double
salt of potassium and sodium sulphate exists of the constant composi-
tion $K_3Na(SO_4)_2$, so-called glaserite. On the other, it has been held
that this name merely covers those members of the isomorphous series
of mixed crystals formed by the two sulphates which contain a
maximum of potassium sulphate. J. H. van't Hoff and H. Barschall[1]
have investigated this point and find no evidence in support of the
view that glaserite has a constant composition.

Gyrolite.—This rare mineral has been observed by E. Hussak[2] in
the form of spherical aggregates composed of thin radial leaflets
occurring in crevices in diabase at Mogy-guassù, São Paulo, Brazil.
The specific gravity is 2·409, and the mineral is uniaxial with negative
double refraction. The composition is very similar to that of gyrolite
from Skye, as shown by the following analysis of white material made
by G. Florence :

SiO₂.	Al₂O₃.	CaO.	Na₂O.	K₂O.	H₂O.	Total.
52·77	0·73	33·04	0·35	0·41	12·58	99·88

Under alumina is included a trace of ferric oxide. A dark green
variety contained 7·36 per cent. $Fe_2O_3 + Al_2O_3$ and 0·32 per cent. MnO.
We may note here that F. Cornu[3] identifies gyrolite from the Hebrides,
Faroë Islands, Greenland, Poonah, and São Paulo with the mineral
described by Pelikan under the name zeophyllite.

Hellandite has already been the subject of a preliminary notice by
W. C. Brögger, who has now[4] published a full account based on the
study of more than forty crystals. The mineral was found in a quarry
opened in a pegmatite vein on the top of a small hill called
Lindvikskollen near Kragerö, Norway. The crystals belong to the
prismatic class of the monoclinic system, and are for the most part a
good deal altered. The freshest consist of nut-brown material with
vitreous lustre, others exhibit various shades of brown, while the most
altered ones consist of a yellow to white earthy mass. The alteration,
which is probably due to hydration, does not seem to have had any
very great influence on the relative proportions of the constituents.
The purest material had the specific gravity 3·67 to 3·70, that of the
substance used for analysis II was 3·41 to 3·33. An analysis (I) by
O. N. Heidenreich made on a small quantity of material has already

[1] *Zeit. physikal. Chem.*, 1906, **56**, 212.   [2] *Centr. Min.*, 1906, 330.
[3] *Centr. Min.*, 1906, 79.   [4] *Zeit. Kryst. Min.*, 1906, **42**, 417.

been published, II and III are due to L. Andersen-Aars ; the material used for III was highly altered :

	SiO_2.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	Ce_2O_3.	Y_2O_3.	Er_2O_3.	ThO_2.
						40·12		
I.	23·55	10·22	2·64					
II.	23·66	10·12	2·56	5·91	1·01	19·29	15·43	0·62
III.	27·88	9·67	2 01	3·13	0·37	19·71	13·26	0·30

	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	·10·05	— —	0·26	0·06	7·55	100·19
II.	9·81	0·10	0·23	0·06	11·75	100·55
III.	9·97	0·13	0·41		13·09	99·93

Since some 6 per cent. of the water was expelled below 500° and the rest only at red heat, it seemed probable that about 5 per cent. was chemically combined. This was confirmed by an experiment on the freshest material, when 4·86 per cent. of water was found. Accepting this value as the true percentage of water, and assuming that the small quantities of potash and soda are due to felspar, the ratios (calculated from II) $R''O : H_2O : R_2'''O_3 : SiO_2$ are very accurately $2:3:3:4$. The formula is therefore either of the type

$$Ca_2R_3'''[R'''(OH)_2]_3[SiO_4]_4$$
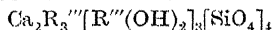
or of the type $Ca_2[R'''(OH)]_6[SiO_4]_4$. Of these two possibilities, Brögger is inclined to prefer the first on the ground of certain analogies which hellandite shows with guarinite, danburite, andalusite, and topaz. Accepting this view, the composition of the mineral may be represented thus : $Ca_2[\frac{2}{3}Al\frac{1}{3}(Mn,Fe)]_3[(Y,Er,Ce)(OH)_2]_3[SiO_4]_4$.

Hibschite.—Reference was made to this mineral last year. A detailed account of its properties and mode of occurrence has recently been published by F. Cornu.[1]

Huebnerite.—Large black crystals from the Comstock mine, Lawrence County, South Dakota, were found by W. P. Headden[2] to have the following composition :

WO_3.	MnO.	FeO.	CaO.	Total.
75·12	20·54	3·01	1·04	99·71

Jadeite and Nephrite.—Some very valuable contributions to our knowledge of these two minerals are to be found in the monumental treatise entitled "Investigations and Studies in Jade,"[5] issued by the executors of Reginald Heber Bishop. In two vast volumes, each weighing about sixty pounds, are embodied the results of a series of studies by leading American experts of the specimens contained in the great Bishop collection now preserved in New York. The mineralogical portion has been edited by G. F. Kunz, and he has had the assistance of S. L. Penfield, F. W. Clarke, J. P. Iddings, C. Palache, L. V. Pirrson, and others. On breaking up a specimen of jadeite, which

[1] *Tsch. Min. Mitt.*, 1906, **25**, 249.   [2] *Proc. Colorado Sci. Soc.*, 1906, **8**, 174.
[5] *Privately printed*, New York, 1906.

probably came from Tibet, two small crystals were found. These closely resembled augite in shape, and enabled Penfield to determine the crystallographic constants of the mineral. He found $a : b : c = 1\cdot103 : 1 : 0\cdot613$; $\beta = 72°44\frac{1}{2}'$. The cleavage angle was 92°58'. The extinction angle measured on (010) was 34° and the optic axis angle 70°, one axis being nearly parallel to the Z axis of the crystal. This specimen had the following composition:

SiO₂.	Al₂O₃.	Fe₂O₃.	MgO.	CaO.	Na₂O.	K₂O.	H₂O.	Total.	Sp. gr.
58·80	25·37	0·33	0·25	0·58	14·65	0·05	0·14	100·17	3·3359

In all, fifty-eight analyses of the two minerals are given, and, with two exceptions, these were made by P. T. Walden and H. W. Foote. In his discussion of the formulæ to be assigned to these minerals, F. W. Clarke advances arguments in support of the view that the molecules of the pyroxenes are more complex than those of the amphiboles, and that jadeite must be represented as $Na_6Al_6Si_{12}O_{36}$. Further, he holds that it is not to be regarded as a metasilicate, but as a mixture of an orthosilicate and a trisilicate. At the conclusion of a paragraph devoted to a discussion of the origin of jadeite considered as a rock, Pirrson says "jadeite is a metamorphosed igneous rock, a member of the phonolite family. The white varieties are probably metamorphosed dikes of the aplitic, leucocratic type, belonging in this family and the darker green types those containing more iron-bearing dark silicates, like tinguaites." The mean value of the specific gravity of all the nephrite specimens was 2·9505; that of the jadeites, including some chloromelanites, was 3·3202.

Janosite.—The existence of this mineral as a separate species has been denied by E. Weinschenk,[1] who on the ground of its optical properties has identified it with copiapite. H. Böckh and K. Emszt, the discoverers of janosite, have, however, reiterated their belief in its individuality, laying special stress on its specific gravity and chemical composition. In his reply Weinschenk states that a comparison of janosite with specimens of copiapite recently received from Copiapo fully confirms his previous conclusion. Further, a specimen of janosite supplied by Böckh was found to contain 30·80 per cent. Fe_2O_3 and to have a specific gravity 2·17, the corresponding values found for copiapite being 31·09 and 2·19 respectively.

Jamesonite.—Imperfect crystals occurring in quartz veins at Sheridan, Pennington County, South Dakota, have been analysed by W. P. Headden.[2] The percentages found are in tolerable harmony with those required for the ordinarily accepted formula, $2PbS,Sb_2S_3$:

S.	Sb.	Pb.	Fe.	Cu.	Zn.	Co.	Insol.	Total.	Sp. gr.
18·90	26·99	51·15	1·30	0·24	0·05	trace	1·13	99·76	5·81304

[1] *Ann. Report*, 1905, 279; *Föld. Közlöny*, 1906, **36**, 224, 228, 359.
[2] *Proc. Colorado Sci. Soc.*, 1906, **8**, 174.

Malacon.—A specimen of this mineral examined by E. S. Kitchin and W. G. Winterson [1] proved to be distinctly radioactive and to contain argon. Taking the radioactivity of uranium oxide as unity, that of the malacon is 0·0161. This value is much greater than can be accounted for by the uranium present in the mineral. After decomposition the radioactivity is entirely associated with the zirconium dioxide. On fusion with potassium hydrogen sulphate, 100 grams of malacon gave 37·91 c.c. of gas, consisting of 33·24 c.c. of carbon dioxide, 2·82 c.c. of argon, 0·94 c.c. of helium, 0·57 c.c. of hydrogen, and 0·34 c.c. of nitrogen. The specific gravity is 3·908, rising to 4·232 after heating. The complete analysis is as follows:

ZrO_2.	SiO_2.	Fe_2O_3.	MgO.	CaO.	U_3O_8.	$(Y,Ce)_4O_3$.	H_2O.
67·78	22·53	4·93	0·70	0·41	0·33	0·09	1·84

If the other constituents are neglected, and zirconia and silica calculated to 100, the percentages obtained agree well with those required for the formula $Zr_3Si_2O_{10}$. The analytical results differ a good deal from those previously recorded for the substance, and from which the formula $3(ZrO_2,SiO_2),H_2O$ has been derived.

Meneghinite.—A fibrous mineral found in the Gorham claim near Rochford, Pennington County, South Dakota, has been analysed by W. P. Headden.[2] The ratios obtained are only approximate, but show that the probable formula is $4PbS,Sb_2S_8$:

S.	Sb.	Pb.	Cu.	Insol.	Total.	Sp. gr.
17·51	18·20	62·85	0·86	0·49	99·91	6·21

Traces of As, Bi, Cd, and Fe are also present.

Naegite.—T. Wada [3] has published some important fresh information about this mineral. He states that a crystallographic examination by Takimoto has shown that in habit and angles the mineral is closely related to zircon, whilst Haga has found that it contains a large quantity of zirconia, a constituent previously overlooked, probably owing to some imperfection in the methods of separation employed. Haga's analysis is as follows:

ZrO_2.	ThO_2.	SiO_2.	$(NbTa)_2O_5$.	UO_3.	Y_2O_3.	Total.	Sp. gr.
55·30	5·01	20·58	7·69	3·03	9·12	100·73	4·091

Petterdite.—Under this name there was described, a few years ago, a mineral from the Britannia mine, Zeehan, Tasmania, which was supposed to be a new oxychloride of lead. A careful re-examination of this substance recently made by C. Anderson [4] has proved that it is merely a variety of mimetite.

[1] *Trans.*, 1906, **89**, 1568.   [2] *Proc. Colorado. Sci. Soc.*, 1906, **8**, 174.
[3] *Beiträge z. Min. Japan*, 1906, No. **2**, 23.
[4] *Rec. Australian Mus.*, 1906, **6**, 133.

Pitchblende.—The pitchblende from which rutherfordine is derived (see p. 310) is 20 per cent. more radioactive than that from Joachimsthal, and has been shown by W. Marckwald[1] to have the following composition :

U_3O_8.	PbO.	CaO.	FeO.	SiO_2.	$H_2O + CO_2$.	Gangue.
87·7	7·5	2·1	1·0	0·3	0·5	0·2

Plumbogummite.—E. Hussak[2] has published the following analysis by G. Florence of a mineral found in the form of pebbles, "favas," in the diamond sands of Brazil :

SiO_2.	PbO.	CaO.	CeO.	Al_2O_3.	P_2O_5.	H_2O.
0·70	35·50	0·62	0·16	24·92	22·50	16·30

The corresponding formula, $2(Pb,Ca)O, 3Al_2O_3, 2P_2O_5, 10H_2O$, is near to that of plumbogummite, although it contains 3 molecules more water.

Pyrochroite.—This rare mineral occurs at Långban in prisms and needles with a distinct basal cleavage. The following analysis, given by H. Sjögren[3] agrees with the formula $Mn(OH)_2$:

MnO.	FeO.	CaO.	MgO.	H_2O.	Sp. gr.
77·3	0·4	trace	1·7	20·9	3·2435

Quartz.—J. G. Königsberger and W. J. Müller[4] have studied the liquid inclusions in quartz crystals from the biotite-protogine of the Aar district. They find that for these crystals there is a constant relation between the volume of the liquid and the volume of the gas in a cavity, a fact first observed by Sorby. On heating at from 200° to 230° the bubbles disappear, the liquid expanding to fill the cavity. They conclude that the included matter represents a homogeneous portion of the liquid phase. Its composition in the case of a specimen from the Büchistock appears to be as follows :

H_2O.	CO_2.	Na.	K.	Li.	Ca.	Cl.	SO_4.	CO_3.
83·4	9·5	2·0	0·7	0·2 ?	0·3	1·6	0·5	1·8

M. Berthelot[5] has found that crystals of amethyst from Brazil decolorised by heating to 300° regain their original tint on exposing them for a few weeks to the action of radium chloride. He attributes this change to the reoxidation of traces of manganese present, and suggests that the colour of amethyst and other minerals may be due to the action of radioactive substances. On heating smoky quartz and green fluor spar, petroleum is driven off, and in these cases the colour is due to organic matter.

Rhodochrosite.—Small rhombohedra {100} of this mineral have been

[1] *Centr. Min.*, 1906, 761. [2] *Tsch. Min. Mitt.*, 1906, **25**, 335.

[3] *Geol. Fören. Stockholm Förhandl.*, **27**, 37. [4] *Centr. Min.*, 1906, 72.

[5] *Compt. rend.*, 1906, **143**, 477.

found at S. Barthélemy, Val d'Aosta, by F. Millosevich.[1] The cleavage
angle is 73°10′, and the composition as follows :

MnO.	FeO.	CaO.	MgO.	CO_2 (diff.).
56·00	2·04	3·33	trace	38·63

Rock Salt.—The blue colour observed in certain specimens of rock
salt has been the subject of much experiment and speculation in recent
years. As pointed out in a paper by F. Focke and J. Bruckmoser,[2] the
explanations offered fall under three main headings. In the first place,
it is held that the phenomenon is a purely physical one due to the pre-
sence of very minute fissures, secondly we have the view that it is due
to the presence of some inorganic colouring matter such as the sub-
chloride of sodium or a compound of iron, and lastly that it is caused
by organic material. It has, however, been shown that the blue colour
can be produced by exposing salt to the action of cathode rays or by
heating it with metallic sodium, and the opinion is now widely held
that the colour is due to the presence of subchloride or of metallic
sodium. Though the latter view does not commend itself to Focke and
Bruckmoser or to E. Pieszczek,[3] who has found a deficiency of chlorine
amounting to as much as 0·4 per cent. in the blue portions, it has
received strong support from the work of H. Siedentopf.[4] This author
investigated specimens of salt, coloured blue by the action of sodium
vapour with the aid of the ultra-microscope and believes that he has
demonstrated the presence of metallic sodium deposited in ultra micro-
scopic fissures in the salt. These particles of sodium may possibly be
covered by a very thin or " molecular " cooling of subchloride which
protects them from the action of reagents such as chlorine. He thinks
that since rock salt strongly absorbs Becquerel rays the blue colour of
the mineral may perhaps be due to the sodium produced by the cumula-
tive effect of the radiation absorbed during long periods of time.

The gases included in certain specimens of salt from Roumania have
been the subject of an interesting investigation by N. Costachescu.[5]
The gases were extracted either by dissolving the salt in well boiled
water or by pulverising it under mercury. The composition of the
gases was found to vary a good deal with the method of extraction
employed, but the following points appear to be established. In the
first place the quantity of gas contained in a given weight of salt varies
greatly, but there is no relation between the quantity of gas evolved
and the solid impurities in the salt. Secondly, as regards the nature of
the gases given off, the specimens examined fall into two groups, those
in which hydrocarbons are predominant and those which yield little else

[1] *Atti R. Accad. Lincei*, 1906, [v] **15**, i, 317.

[2] *Tsch. Min. Mitt.*, 1906, **25**, 43.   [3] *Pharm. Zeit.*, **51**, 700.

[4] *Phys. Zeit.*, 1905, **6**, 8 5.   [5] *Ann. Sci. Univ. Jassy*, 1906, **4**, 3.

but nitrogen, a gas which is invariably present. Oxygen is also always found, but in smaller proportion than the nitrogen and there is no constant relation between the quantities of these two elements. Carbon dioxide is either absent or occurs in very small quantities. Argon could not be detected. Methane is almost always present, but the higher hydrocarbons appear to be absent. To account for these facts the author suggests that the gases have been derived mainly from the decomposition of the microscopic fauna of the lagoon in which the deposits were laid down, and to but a limited extent from the atmosphere through the medium of the solvent. The absence of carbon dioxide and argon can be explained in this way, but it is difficult to account satisfactorily for the oxygen always observed.

Sarcolite.—Specimens of this mineral from Vesuvius have been submitted to a careful crystallographic and optical examination by A. Pauly.[1] Two pure crystals were used for analysis :

SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	Total.	Sp. gr.
39·34	21·63	33·70	0·36	4·43	traces	99·46	2·7

Scheelite.—The crystals from Traversella have been measured by L. Colomba[2] who moreover has analysed specimens of different colours in order to test Traube's hypothesis that the ratio $a : c$ varies with the amount of molybdic acid present. His results are as follows :

	WO_3.	MoO_3.	CaO.	MgO.	Total.	$a : c$.
I. Colourless crystals	77·03	3·15	19·73	– –	99·91	1·5398
II. Reddish-brown crystals	77·35	2·46	18·33	1·67	99·81	—
III. Greenish-brown ,,	78·75	1·47	19·23	0·55	100·00	1·5352
IV. Orange ,,	79·68	0·72	19·43	trace	99·83	· –

Since the mean value of c calculated from measurements of crystals of the composition given under I and III falls about midway between those accepted by Traube for pure scheelite and pure calcium molybdate respectively, this work affords no confirmation of the view that a regular variation takes place.

Siderite.—Minute crystals from Frostburg, Maryland, have been shown by W. T. Schaller[3] to be pure ferrous carbonate. An analysis made on 0·1 gram of carefully selected material gave 62·01 per cent. of iron (calc. 62·07 per cent.). MnO, CaO, and MgO were proved to be absent. A number of measurements of the crystals were made for the purpose of defining accurately the ratio $a : c$ for pure siderite. The mean value deduced is $c = 0·8241$. This corresponds to a cleavage angle $rr' = 73°18·6'$ and differs considerably from that hitherto adopted for the mineral, namely, $c = 0·81841$, $rr' = 73°0'$.

[1] *Centr. Min.*, 1906, 266.   [2] *Atti R. Accad. Lincei*, 1906, [v], **15**, i, 281.
[3] *Amer. J. Sci.*, 1906, [iv], **21**, 364.

Stibiotantalite.—This very rare mineral was originally described by G. A. Goyder as occurring in water-worn fragments at Greenbushes, Western Australia. Crystals have been discovered in recent years at Mesa Grande, San Diego County, California, associated with tourmaline, pink beryl, quartz, orthoclase, and lepidolite, and have been the subject of an exhaustive investigation by S. L. Penfield [1] and W. E. Ford. The mineral is an isomorphous mixture of $(SbO)_2Cb_2O_6$ and $(SbO)_2Ta_2O_6$, and has a specific gravity varying from 5·98 to 7·37, depending on the relative proportions of columbium and tantalum present, and diminishing as the amount of the latter decreases. It crystallises in the hemimorphic class of the orthorhombic system, though owing to twinning the crystals simulate holohedral symmetry. In axial ratio and habit it shows relations with columbite. Owing to its yellow colour, high index of refraction, and good cleavage it might be mistaken for blende. In the following table I is the original analysis of the Australian mineral, II and III are each the means of two concordant analyses made on separate crystals of the Mesa Grande material.

	$(Ta,Cb)_2O_5$.	Sb_2O_3.	Bi_2O_3.	NiO.	H_2O.	Total.	Sp. gr.
I.	58·69	40·23	0·82	0·08	0·08	99·90	7·37
II.	55·33	44·26	0·33	—	— - -	99·92	6·72
III.	50·30	49·28	0·53	—	—	100·11	5·98

Tapiolite.—A group of distorted crystals found by W. P. Headden [2] in granite near Custer City, South Dakota, were shown by S. L. Penfield to be tetragonal pyramids {111} with small {201} planes. Two analyses were made :

	FeO.	Ta_2O_5.	Cb_2O_5.	WO_3.	SnO_2.	Cassiterite.	Insol.	Total.
I.	16·85	78·61	4·29	0·11	0·07	0·31	- - -	100·24
II.	15·60	78·58	3·90	0·59		- -	1·29	99·96

Traces of TiO_2 were found in analysis I and there is reason to believe that FeO is too high. The formula is $FeTa_2O_6$, a portion of the tantalum being replaced by columbium and taken in conjunction with the crystallographic characters shows that the substance is tapiolite. The specific gravity 7·2185 is low for a compound containing so little columbic acid. This point is discussed by Headden, who finds himself unable to explain it.

Tetrahedrite.—In the course of a description of the mines and minerals of the Val de Villé (Weilerthal), Alsace, Ungemach [3] has given the results of an elaborate crystallographic investigation of the beautiful crystals of tetrahedrite found at the Sylvester mine. Two different types of crystals can be readily distinguished. One (analysis I below), rich in arsenic but poor in silver, is met with in the upper portions of the veins; the other, found at greater depths, is rich in silver and poor in arsenic (analysis II).

[1] *Amer. J. Sci.*, 1906, [iv], **22**, 61.   [2] *Proc. Colorado Sci. Soc.*, 1906, **8**, 177.
[3] *Bull. Soc. franç. Min.*, 1906, **29**, 194.

The comparatively large quantities of Zn and Bi present are some-what remarkable, and the author is inclined to believe that they are due to the presence of native bismuth and of zinc blende. Be this as it may, if the formula is calculated omitting zinc, it is found that the ratio $R''S : R_2'''S_3$ is $3.07 : 1$ for I and $3.21 : 1$ for II.

The variety of tetrahedrite previously described under the names *coppite* and *frigidite* has been examined by E. Manasse.[1] Three specimens were analysed. The results, which are given below, analyses III, IV, and V, are in harmony with a formula of the type

$$3R'_2S, R'''_2S_3 + x6R''S, R'''_2S_3.$$
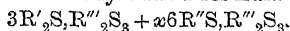
Traces of tin were found in IV and V.

	Cu.	Ag.	Pb.	Fe.	Zn.	Ni.	As.	Sb.	Bi.	S.	Total.	Sp. gr.
I.	38·15	trace	0·53	3·77	5·05	—	6·75	17·47	1·63	25·58	98·93	4·82
II.	34·15	5·94	—	3·79	4·86	—	1·21	25·24	—	25·22	100·41	5·10
III.	37·42	—	trace	6·60	1·72	0·23	trace	29·28	—	25·70	100·95	—·
IV.	37·54	—	trace	6·01	1·98	0·14	trace	29·54	—	25·48	100·69	—
V.	30·04	—	0·26	9·83	0·59	3·46	1·50	28·82	—	24·48	98·98	—

Thuringite.—F. Kretschmer[2] has published further details as to the occurrence of this mineral at Gobitschau, and has given three new analyses.

Thorianite.—In a paper published last year, W. R. Dunstan and G. S. Blake suggested that the intimate association of thoria with oxides of uranium might be a case of isomorphous mixture. This view has been confirmed by a series of analyses of thorianite from the Galle district of Ceylon, recently published by W. R. Dunstan and B. M. Jones.[3] Their results show that the proportion of the two oxides present in the mineral may vary considerably, as can be seen on comparing columns I to VII of the following table. I gives the composition of small crystals from Hinidumpattu, Galle District; II to VI that of large lumps from the same locality, II, III and IV being different portions of the same crystal; VII is an analysis of a large crystal of the ordinary variety from Balangoda. All the speci-mens contained helium and carbon dioxide. The radio-activity of specimen I was compared by R. J. Strutt with that of the mineral the composition of which was given last year and found to be 1·16 times as great. Column VIII contains some determinations of the more important constituents of thorianite made by E. H. Büchner[4] in Sir W. Ramsay's laboratory in the course of an investigation into the distribution of the radioactivity among the constituents of the mineral. In addition to the elements enumerated, small quantities of copper, tin, antimony, bismuth (?), aluminium, titanium, and zirconium were estimated, and traces of mercury, arsenic (?), cadmium (?) and phos-

[1] *Mem. Soc. Tosc. Sci. Nat.*, 1906, **22**, 81.

[2] *Centr. Min.*, 1906, 309.

[3] *Proc. Roy. Soc.*, 1906, **77**, *A*, 546.

[4] *Ibid.*, **78**, *A*, 385.

phorus observed.   One gram of the mineral yielded 8·2 c.c. of helium.
The radioactivity is associated almost entirely with the portion of the
mineral soluble in nitric acid.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
ThO₂	58·84	62·16	66·82	—	62·32	63·36	78·98	70·96
(Ce,La,Di)₂O₃	0·85	1·84		—	2·24	1·16	1·47	1·96
UO₂	32·74	10·32	28·24	28·68	27·02	27·99	13·40	13·12ˣ
UO₃		18·88						
PbO	2·56	2·29	2·29	2·50	2·99	2·90	2·54	2·42
Fe₂O₃	1·31	1·11	1·22	2·43	2·28	1·27	0·87	2·05
CaO	0·19	0·59	0·54	—	0·50	0·85	0·91	0·13
H₂O	1·26	1·05	1·00	- -	2·16	1·32	1·28	3·20
Insol. in HNO₃	0·45	0·77	0·56	0·54	0·87	0·77	0·47	—

* U_3O_8.

Titanite.—F. Zambonini[1] called attention last year to the unsatis-
factory state of our knowledge of the composition of titanite.   He has
recently returned to this question, and has pointed out that the com-
position of specimens containing tervalent elements is better expressed
by Blomstrand's formula, $2(R_1''R_2'''O_2, TiO)O.SiO_2$, than by that due to
Groth, who regards such titanites as consisting of isomorphous
mixtures of $CaTiSiO_5$ and $R_2'''SiO_6$.   Blomstrand's formula represents
titanite as containing titanyl, TiO, playing the part of a cation thus,
$TiO:O_2SiO_2:Ca$, aluminium, iron, yttrium, and cerium entering the
molecule in the bivalent grouping $R_2''O_2$.   As, however, recent work
on titanium, zirconium, and tin has shown that these elements readily
form complex anions, Zambonini thinks that it will be more in
harmony with what is known of the general chemical character of
titanium if it is regarded as playing a similar part in titanite.   He
therefore proposes to modify Blomstrand's formula in this sense, and
regards the mineral as the calcium salt of a complex silicotitanic acid
$TiO:SiO_4:Ca$.   The tervalent elements enter the molecule as two uni-
valent groupings $R'''O$, replacing TiO.

Zeolites.—Certain zeolites which occur in the amygdaloidal basalt of
the Debarea plateau, Eritrea have been described by E. Manasse.[2]
Two specimens of *chabazite* had a composition agreeing with the
formula $CaAl_2Si_4O_{12}, 6H_2O$.   Analyses I. and II.   Crystals of *apophyllite*,
measured by G. D'Achiardi, agreed approximately with the formula
$H_7KCa_4(SiO_3)_8, 4\frac{1}{2}H_2O$.   Analysis III.   The loss of water at various
temperatures and its reabsorption on standing in moist air were
studied in the case of both minerals.

E. Manasse[3] has also re-examined the mineral from Montecatini
termed *picrothomsonite* by Meneghini and A. D'Achiardi, and has come
to the conclusion that it is *thomsonite*.   The mean composition derived
from two concordant analyses is given under IV below.   Associated with

1   *Atti R. Accad. Lincei*, 1906, [v.], **15**, i, 291.
2   *Proc. verb. Soc. Tosc. Sci. Nat.*, 1906, **15**, 65.
3   *Ibid.*, 20.

this substance is another called *sloanite* by Meneghini. This appears to be identical with *natrolite*. Analysis V.

	SiO₂.	Al₂O₃.	CaO.	MgO.	K₂O.	Na₂O.	H₂O.	Total.
I.	48·35	19·47	8·77	0·20	trace	1·05	22·13	99·97
II.	46·69	20·27	9·72	—	trace	0·96	22·80	100·44
III.	52·84	trace	24·46	—	5·42	trace	16·48	99·20
IV.	36·90	31·36	14·48	0·33	0·65	3·81	13·59	101·12
V.	46·49	25·47	1·10	trace	trace	17·05	9·76	99·87
VI.	65·21	11·20	3·77	trace		6·07	14·22	100·47

G. D'Achiardi [1] has referred to *ptilolite*, a mineral from San Piero in Campo, Elba, which has the composition given under VI, and has suggested that the mineral called *hydrocastorite* is possibly identical with a pulverulent form of *stilbite*, containing small quantities of lithium, which he has found at the same locality. He has also given some further account of the zeolite which was mentioned last year as probably constituting a new species.[2]

Zoisite.—Striated prisms associated with prehnite have been found at the Trace mine, Juarez district, Lower California. The optical characters have been studied by O. C. Farrington,[3] and the mineral has been analysed by H. W. Nichols. Analysis I below.

The numbers obtained agree well with the formula $H_4Ca_4Al_6Si_6O_{27}$, which is that usually accepted for zoisite with the addition of one molecule of water. There is good evidence for believing that in this case the extra molecule of water is a primary constituent of the mineral, and not the result of alteration, and the authors quote other similar instances. Traces of K and Na were also present.

Analysis II, which agrees with the ordinary formula, was made by E. Manasse,[4] on a specimen from Monte Corchia, Alpi Apuane.

	SiO₂.	Al₂O₃.	Fe₂O₃.	MnO.	CaO.	MgO.	H₂O.	Total.
I.	38·15	29·50	4·60	0·55	22·71	0·63	3·76	99·90
II.	37·86	26·88	7·90	---	24·65	---	2·07	99·36

Radioactivity of Minerals.

The radioactivity of minerals containing thorium has occupied the attention of several workers.

B. B. Boltwood [5] has examined thorianite, thorite, orangite, and monazite, containing 78·8, 52, 51·1, and 4·66 per cent. of ThO₂ respectively. He has found that the activity of one gram of thoria was practically the same in each of the four minerals. He believes that his results confirm the view that radio-thorium is a disintegration

[1] *Mem. Soc. Tosc. Sci. Nat.*, 1906, **22**. [2] *Ann. Report*, 1905, 282.
[3] *Field Columbian Mus. Pub.*, 112; *Geol. Ser.*, **3**, No. 4, 55.
[4] *Proc. verb. Soc. Tosc. Sci. Nat.*, 1906, **15**, 20.
Amer. J. Sci., 1906, [iv], **21**, 115.

product of thorium, but that they do not lend any support to the idea that the activity of thorium in a mineral depends on the amount of uranium present. On the other hand, the available data point to the conclusion that the quantity of actinium in a radioactive mineral is proportional to the uranium present. Similar conclusions as to the proportionality existing between the activity of thorium minerals and their thorium content have been arrived at by H. M. Dadourian [1] and by H. N. McCoy and W. H. Ross. [2]

Finding reason to suspect that their former estimate of the amount of radium associated with a given quantity of uranium in a mineral was too high, E. Rutherford and B. B. Boltwood [3] have repeated the estimation. They now find that approximately 3.8×10^{-7} grams of radium are associated with 1 gram of uranium, a result about half that previously obtained. They point out that a ton of 60 per cent. uranium ore would carry radium equivalent to about 0.35 gram of radium bromide.

Special Reactions of Minerals.

F. Cornu [4] has examined and tabulated the behaviour of a large number of minerals when finely powdered, moistened, and brought in contact with neutral litmus paper. He finds that all the minerals of the kaolin and pyrophyllite groups show acid reaction, and that the same is true of opal. On the other hand, olivine, mesolite, and talc react alkaline. The same writer [5] bases a method of distinguishing between calcite and dolomite on the behaviour of these substances towards water containing phenolphthalein. On shaking the solution with finely-divided calcite a dark red colour is produced, whilst dolomite gives merely a faint red tinge. V. Goldschmidt [6] has called attention to the ease with which a number of minerals can be determined by finding the loss of weight they suffer on ignition. Experiments made under his direction by P. Hermann on a number of zeolites show that these substances can be rapidly identified by heating quantities of from 30 to 100 milligrams in a platinum spoon over a spirit lamp.

Meteorites.

The composition of a number of meteorites has been examined during the past year. Among these we may notice the following :

Canon Diablo.—A septarian nodule found in this meteorite has been studied by W. Tassin. [7] The septa are metallic and like the mass of

[1] *Amer. J. Sci.*, 1906, [iv], **21**, 427.   [2] *Ibid.*, 433.   [3] *Ibid.*, 1906, **22**, 1.
[4] *Tsch. Min. Mitt.*, 1906, **24**, 417.   [5] *Centr. Min.*, 1906, 550.
[6] *Jahrb. Min.*, 1906, i, 16.   [7] *Proc. U.S. Nat. Mus.*, No. 1497.

the iron. The interseptal portions are made up of crystalline graphitic and amorphous carbon mixed with troilite. A lustrous metallic substance consisting mainly of iron (88·8 per cent.), but containing nickel, silicon, carbon, phosphorus, and a trace of cobalt, is also present.

Coon Butte.—This aerolite was discovered in 1905 by D. M. Barringer near Coon Butte, Coconino County, Arizona. There is some evidence to show that its fall was observed in January, 1904. Its general appearance and the results of an optical examination made by G. P. Merrill suggest affinities with the meteorites from Ness County, Kansas, or with the Pultusk meteorite. J. W. Mallet [1] has found that it consists mainly of enstatite and olivine, but it also contains maskelynite and nickel-iron. The composition of all these constituents has been ascertained, and traces of tin and copper found in the last.

Estacado.—An aerolite fell in 1882 near Estacado, on the staked plains of north-western Texas. It has been investigated by J. M. Davison,[2] who has determined the composition of the metallic portion, which amounts to 16·41 per cent., and of the stony matter, which appears to be mainly olivine and enstatite.

Kangra Valley.—An aerolite which is reported to have been seen to fall in the Kangra Valley, Northern Punjaub, has been described by W. N. Hartley.[3] The specimen, which weighs 350 grams, appears to consists of a crystalline ground mass of enstatite and olivine, through which are scattered numerous metallic grains. A spectroscopic examination of the metallic portion showed the presence of Fe, Ni, Co, Cr, with small quantities of Cu, Ag, Pb, and Ga. Traces of Mn, Ca, K, and Na were also detected. Ca and Mg are the principal constituents of the siliceous portion, accompanied by minute quantities of Fe, Ni, Cr, Ga, Sr, Pb, Ag, Mn, K, and Na.

Kodaikanal.—A new silicate, weinbergerite, has been discovered by F. Berwerth in this meteorite (see page 310).

Modoc.—A fall of meteorites took place on the night of September 2, 1905, in the vicinity of Modoc, a small town in Scott County, Kansas. Fourteen specimens, mostly complete individuals, have been recovered, and the largest of these, weighing 4·64 kilos, now in the possession of the U.S. National Museum, has been described by G. P. Merrill.[4] Under the microscope it is seen to consist essentially of olivine and enstatite, with blebs of metallic iron and troilite. It belongs to Brezina's group of veined chondritic meteorites. Analyses of the metallic portion and of the soluble and insoluble silicates have been made by W. Tassin.

[1] *Amer. J. Sci.*, 1906, [iv], **21**, 347.

[2] *Ibid.*, 186 ; **22**, 55.

[3] *Trans.*, 1906, **89**, 1566.

[4] *Amer. J. Sci.*, 1906, [iv], **21**, 356.

Shelburne.—A second stone of this fall has been described by O. C. Farrington.[1]

South Bend.—O. C. Farrington[1] has also examined a pallasite weighing $5\frac{1}{2}$ lb, found in 1893 near South Bend, St. Joseph County, Indiana, and refers it to the Imilac group.   The ratio of nickel-iron to chrysolite is 21·4 to 78·6.

In conclusion, it should be noted that a great deal of interesting information regarding Japanese meteorites has been brought together by K. Jimbŏ[2]

<div align="right">A. Hutchinson.</div>

[1] *Field Columb. Mus. Pub.*, 109 ; *Geol. Ser.*, **3**, 2.

[2] *Beiträge z. Min. Japan*, 1906, No. 2, 30.

RADIOACTIVITY.

The year's work has been notable for the very large number of important investigations, with interesting theoretical bearings, but chiefly concerned with points of detail rather than with any great general extension of the boundaries of the subject. Radioactivity at the present time resembles somewhat the science of organic chemistry in its early days, both in its bewildering wealth of detail and in the opportunities it affords for the crucial examination of theoretical predictions. On this account, however, it becomes increasingly difficult to give any connected account of the progress made. The various investigations in different parts of the subject are so closely interconnected that they cannot well be separated into distinct sections, and some latitude in the order in which the subjects are taken must be allowed. It is impossible to draw a distinction between researches which are more nearly physical and those which are mainly of chemical interest, for it seems that the more clearly an investigation falls under the one head the more surely does it become indispensable to the other side of the subject. Thus the electro-chemical researches, particularly of von Lerch, on the separation of successive disintegration products are indispensable to physicists in the analysis of the complex radiations, and the determination of the physical constants of each type of radiation separately. Bragg's work on the ionisation ranges of the α-rays, dealt with at length last year,[1] has developed this year in the hands of Hahn into a method of analysis of two successive products hitherto regarded as single, and which so far chemical methods have proved powerless to separate. Rutherford's final results, to be considered at length, on the constants of the α-particle, threaten to raise again the problem of the atomic weights of the inert gases, and the validity of the theoretical grounds on which the accepted values are based, whilst Bragg's method of ionisation ranges, as already indicated, affords a novel and independent method of determining the atomic weight of gases. In the wealth of information concerning the properties of each of the new separate disintegration products, now become too numerous almost to remember, no detail is too unimportant to be dealt with, for at any moment some

[1] *Ann. Report* 1905, 295.

such apparently trivial fact may furnish a clue to the laws underlying the arbitrary and mysterious courses along which the devolution of matter is proceeding before our eyes.   Already it is becoming increasingly evident that there is familiar method in the apparent madness, and in the strange resemblances and analogies between the successive members from different parent elements we have a new and varied phase of the old problem of the relations between the elements themselves which finds its most complete expression, although no explanation, in the Periodic Law. When it is considered that each of these disintegration products is a new elementary form of matter and that the total number of elements known has been increased by nearly one-fourth through the study of radioactivity in the last five years, we have a sufficient answer to the view the writer has heard expressed that radioactivity is outside the sphere of chemistry and must be considered the exclusive territory of the physicist.   Since all the newcomers are derived from and related to two only of the previously known elements, it may be realised how little the possibilities of matter have been exhausted by the older chemistry.   But the prospect of any simple and complete hypothesis of matter seems to have been rendered more remote rather than brought within measurable distance of realisation by the recent extensions.

Constants of the α-particle.—Some of the problems in connexion with the nature of the α-ray will be first considered, as these have again occupied a prominent place in the year's work. The controversy[1] between Becquerel on the one hand[2] and Rutherford[3] and Bragg[4] on the other has been satisfactorily settled.   In a later communication, Becquerel[5] gives the results of further experiments in which a beam of α-rays, deflected in a magnetic field, was made to register its deflection on a photographic plate both after passage through a thickness of aluminium foil and when the foil was removed, and he obtained the same result as in Rutherford's experiments, that the beam is more easily deviated after passage through aluminium foil, and therefore suffers retardation of velocity in its passage through matter.   The earlier view that there was an increase in the radius of curvature along the trajectory is shown by the new experiments to have been erroneous, and the traces conform to a circular trajectory.

Rutherford[6] reproduces photographs of a very striking character, showing clearly the displacement of the trace in the direction of greater deviability when the α-rays are caused to pass through 0·003 cm. of aluminium foil, using the homogeneous α-radiation from

[1] *Ann. Report*, 1905, 302.
[3] *Phil. Mag.*, 1906, [vi], 11, 166.
[5] *Compt. rend.*, 1906, 142, 365; *Phil. Mag.*, 1906, [vi], 11, 722; *Phys. Zeit.*, 1906, 7, 177.
[2] *Compt. rend.*, 1905, 141, 485.
[4] *Ibid.*, 627.
[6] *Loc. cit.*

radium C, whilst in another photograph the broad diffuse trace obtained by using a thick layer of a radium salt, emitting several types of α-rays travelling with different velocities, is contrasted with the result when a homogeneous source of α-rays is employed. In addition, the photographs establish a slight but distinct *scattering* of the beam consequent upon its passage through matter. Thus in one photograph the impressions produced by the rays of radium C, (1) in a vacuum, (2) after passage through air, are contrasted, and it is clear that not only can the rays be deviated to a greater extent, but the trace is broader and less well defined in the second case than in the first. This is an important result, as Bragg and Kleeman [1] had shown that if any such scattering in passage through matter occurs it can only be small, and is sharply to be distinguished from the very marked scattering that is shown by the β-rays.

Rutherford,[2] in a paper entitled "The Retardation of the α-Particle in passing through Matter," gives some data differing somewhat from the preliminary measurements already given.[3] It will be recalled that there exists a certain sharply defined "critical velocity" at which all action of the α-ray abruptly ceases, so that even although it is moving at great speed it produces no ionising, photographic, or fluorescent action. This critical velocity is now given as $0·43\ V$, where V indicates in all cases the initial velocity at which the α-particle of radium C, the fastest of those from radium, is expelled. It was found when successive thicknesses of aluminium foil were placed over the source of α-rays that each layer caused a reduction of velocity by an amount greater than the last, but the simple law was established that the diminution of the kinetic energy, or the square of the velocity, of the α-particle was the same amount for each layer of foil added. If the kinetic energy is plotted against the thickness of matter traversed, a straight line is obtained which if produced cuts the axis of zero energy at a point represented by $8·31$ centimetres of air, that is, $1·25$ cm. beyond the critical distance at which the rays cease abruptly to ionise. This has proved a very useful result, although it may be said at once that we have at present no knowledge of what becomes of the α-particle after it has passed through its critical distance. Bronson [4] made a search for any small ionisation by the α-rays beyond their critical distance, but with negative results. The drain on the energy of the α-particle on account of ionisation ceases after the critical distance is passed, so that unless other actions, of which we have at present no knowledge, occur, there may be no cause acting to retard the velocity further once the critical velocity is reached. J. J. Thomson [5] has

[1] *Ann. Report*, 1906, 297.
[2] *Ann. Report*, 1906, 300.
[3] *Proc. Camb. Phil. Soc.*, 1906, **13**, 212.
[4] *Phil. Mag.*, 1906, [vi], **12**, 134.
[5] *Phil. Mag.*, 1906, [vi], **11**, 806.

suggested that the most probable cause of the loss of ionising power by the α-particle is that below the critical velocity it retains an electron and becomes an uncharged atom.[1]

If r is the range of any α-particle in air, its energy is proportional to $r + 1·25$ and its velocity to $\sqrt{r + 1·25}$. The ratio of the velocity of two particles with ranges r_1 and r_2 respectively is therefore $\sqrt{\dfrac{r_1 + 1·25}{r_2 + 1·25}}$. In this way Rutherford has calculated, in terms of that of radium C as V, the velocities of each of the α-particles expelled by radium and its products, using the ionisation ranges as determined by Bragg. These are: Radium, $0·750$ V ; emanation, $0·814$ V (see p. 344) ; radium A, $0·858$ V ; radium F (polonium), $0·787$ V. These results agree closely with the direct measurements about to be considered.   From the scattering of the α-rays in passage through matter it was deduced that some of the rays must suffer a deflection of at least $2°$ from their course, which is equivalent to the effect of an electric field of a hundred million volts per centimetre (compare preceding footnote).

After four years' efforts, Rutherford has now obtained satisfactory measurements of the electrostatic as well as of the electromagnetic deviations suffered by the α-particle.[2]   The former gives the value mv^2/e and the latter the value mv/e, so that from the combined results the velocity v and the ratio e/m of the charge to the mass of the particle can be deduced.   The α-rays of radium C, from an uncovered wire made active by exposure to the emanation, were taken as the standard, and the values in other cases deduced by comparison with this standard. The initial velocity of the α rays from radium C, designated by V previously, is given as $2·06 \times 10^9$ cm. per second, and the ratio e/m as $5·07 \times 10^3$.   These values are both somewhat lower than those previously given from more or less indirect data, and for the future they must be taken as the most trustworthy determinations of these important and difficultly determined constants.

Rutherford next proceeded to examine whether the ratio e/m is the same for all α particles, and whether it is altered by passage of the α particle through matter.   Direct determinations of the electrostatic and magnetic deviation of the α particle of radium C after passing through various thicknesses of matter showed that the ratio e/m is constant within the limit of experimental error.   Similar direct deter-

[1] The assumption seems to be made here that only electrical forces are acting in the collision of the radiant α-particle with the molecules of obstructing matter. But this view presupposes that an uncharged radiant atom would neither ionise nor be retarded or deviated in its passage through matter, an assumption which is far from proved.

[2] *Phil. Mag.*, 1906, [vi], **12**, 348.

minations were also made of the α-particles of radium A, radium F, and actinium B, and, in conjunction with Dr. Hahn,[1] of the α-rays from the excited activity of thorium (thorium B and thorium C, p. 342). An independent determination in the case of radium F or polonium has been carried out by Huff[2] in continuation of the work of A. Stanley Mackenzie. The general result goes to show that the ratio e/m is the same for all the α-particles within the limits of experimental error.

Lastly, the evidence is considered by Rutherford as to the connexion between the α-particle and the atom of helium. All the radio-elements expel α-particles which are identical in all respects save initial velocity of expulsion, and it is pointed out that whatever its nature the α-particle must be a fundamental constituent of the atoms of all the radio-elements. Now the new value for e/m, $5\cdot07 \times 10^3$, is almost exactly one-half that of the hydrogen ion in electrolysis (10^4), and since the atomic weight of helium is accepted as 4, the helium atom, if it carried the single ionic charge carried by the hydrogen ion, would have the value $2\cdot5 \times 10^3$ for the ratio e/m, or one-half that of the α-particle. Several possibilities are discussed by Rutherford, and two may be here considered. The α-particle may be a helium atom with twice the ionic charge, or it may be one-half the chemical atom carrying a single charge. The first alternative is that favoured by Rutherford. Another possibility not discussed is that there is a flaw in the reasoning which has led in the case of the inert gases to the density being doubled to give the atomic weight. Beyond the general evidence already discussed[3] in favour of regarding helium as a general product of radioactive matter, and therefore that the α-particle is or becomes an atom of helium, there is very little actual evidence at the present time on which to base a conclusion. A large number of calculations in radioactivity are based on the hitherto unquestioned assumption that the α-particle carries the single ionic charge, and if that assumption is abandoned, not only are the values of these calculations affected, but in addition much of the foundation on which the atomic theory of electricity has been based is weakened, for the existence of multiple charges, not confined to two units only, may be postulated in many other cases. Until the question is settled, doubt is thrown upon most of the calculated constants in radioactivity, for example, the number of α-particles expelled from a known weight of a radioactive substance in unit time, the periods of average life of the parent elements, the quantity of the disintegration products associated with the parent in state of radioactive equilibrium, &c., which must be either doubled or halved on the view that the α-particle carries two ionic charges. Rutherford calculates, on the latter assumption, the period

[1] *Phil. Mag.*, 1906, [vi], **12**, 371.   [2] *Proc. Roy. Soc.*, 1906, **78** A, 77.

[3] *Ann. Report*, 1905, 303.

of past time required for the generation of the helium in two minerals, thorianite and fergusonite, and arrives in each case at about the same result, namely 400 million years, which brings vividly into prominence the slowness of radioactive change and the extraordinary delicacy of our present means of investigation.

a-Ray Ionisation.—The phenomenon of " initial recombination " discovered by Bragg and Kleeman working with the α-rays of radium [1] has been the subject of a further investigation by Kleeman,[2] who has made the important discovery that the effect appears to be confined to ionisation produced by the α-rays alone. Gases ionised by the action of X-rays, β-rays, and γ-rays do not show the effect, and this is attributed to the relatively low velocity of the α-particle, and the consequently less violent character of the separation of the charged ions from the neutral atom in this case. The view that in α-ray ionisation the electron detached from the atom ionised travels at a low speed, and so is more readily dragged back into, or recombines with, the parent atom by the electric field existing between them, after the α particle has passed, is supported by the fact that the α rays produce no secondary radiation where they impinge, whereas the other radiations give rise to strong secondary radiation known to consist of electrons moving with great velocity. It was found that the effect of the initial recombination was the greater the lower the velocity of the α-particle.

Bragg[3] has attacked an important problem in the nature of ionisation, namely, the determination of the relative total number of ions produced by the α rays in various gases. Several distinct factors have to be considered separately in ionisation by α rays. The ionisation per unit length of path of the α particle, or the specific ionisation, increases with the distance traversed up to the critical velocity, and therefore with diminishing velocity and energy the α particle becomes a more efficient ioniser right up to the point at which it ceases to ionise. Combining with his earlier results the direct measurements of the velocity by Rutherford, it appears that the ionisation increases inversely as the velocity. Since we have seen that the energy lost by the α-particle in traversing unit length of path (in aluminium) is constant, it may be inferred that the energy required to produce an ion cannot be constant, but must be greater at the beginning than at the end of the course of the α-particle.

The range of the α particle in any gas, or conversely the " stopping power " of the gas, is easily measured to very great accuracy, and is simply proportional to the number of molecules in the layer of gas,

[1] *Ann. Report*, 1905, 298.   [2] *Phil. Mag.*, 1906, [vi], 12, 273.
[3] *Trans. Roy. Soc. S. Australia* 1906, 30, two papers ; *Phil. Mag.*, 1906, [vi], 11, 617. ; 1907, [vi], 13, 333.

and with this reservation is not affected by pressure and temperature, and is independent of the chemical nature of the gas. It is a strictly colligative or additive property depending only on the number and nature of the individual atoms. The stopping power of different atoms is very nearly proportional to the square root of the atomic weight, but there is a slight systematic departure from this law, the value being more accurately expressed by $a \sqrt{w} + b w$ than by $a \sqrt{w}$ simply, where a and b are two constants the same for all the elements. Bragg considers stopping power more nearly a purely additive property of the atom than any other save mass. The proportionality of stopping power to the atomic square root is an effect quite apart from its additive nature, and the divergence from exactness is only marked for light atoms below 30, an effect which is curiously similar to the case of the atomic heats.

The total ionisation produced by the α-particle in different gases is a very difficult quantity to measure accurately, and, as is evident from the papers, a great deal of experimental skill has been spent on this part of the problem. The method employed is to determine the specific ionisation at some defined point on the curve connecting ionisation with distance from the source, and that point to which the rays from radium A (the second most penetrating type) just fail to penetrate was selected. The product of this quantity into the range of the α-particle in the gas in question gives a measure of the desired total ionisation, by means of which different gases can be compared together. Initial recombination was carefully guarded against by the use of extremely high voltages, which previous work had shown were necessary in many of the complex gases to produce complete saturation. It was definitely proved that the total ionisation in different gases was very different from that in air, being in the majority of gases tried about one-third higher. Thus the value in the case of carbon disulphide is 1·37 times air, and this is one of the highest determined. Then in order come pentane, methyl iodide, ethyl ether, ethyl chloride, carbon tetrachloride, chloroform, ethyl iodide, ethylene, and lastly acetylene with the value 1·26. The simple gases carbon dioxide, nitrous oxide, and hydrogen are very similar to air. The specific molecular ionisation, or the relative ionisation produced in the molecule by the passage of an α-particle of defined speed, obtained from these data is shown by Bragg to be closely related to other physical constants, such as molecular volume, molecular refractive power, and more closely still to Sutherland's molecular-volume constant B. Thus, although range is strictly additive, capacity for being ionised is a constitutive property of the molecule, and the energy required to produce an ion is not constant. This shows that in the special case of ionisation by radiant

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atoms or α-particles, the act of ionisation is not entirely a sub-atomic process whatever it may be in other cases.[1]

Initial recombination is an effect which varies greatly for different gases and, as Kleeman has also shown, with the speed of the α-particle. There does not appear to be any evidence against the view that a molecule which has already lost one ion or electron is any the less likely to be again ionised, or, in other words, there seems no evidence against the existence of gaseous ions with multiple charges, as concluded by Rutherford in the case of the α-particle itself.

In the same paper, Bragg draws attention to a suggestive fact also commented on by Rutherford independently.[2]   The number of ions made in a day by radium would occupy the same volume approximately as the hydrogen and oxygen generated in the same time by the radium in aqueous solution. In other words, if the saturation current capable of passing through a gas ionised by radium were passed also through a water voltameter in series, the gas generated in the voltameter would be nearly equal in volume to the gas generated by the same radium in aqueous solution.   The question naturally arises whether the hydrogen and oxygen liberated are not actually the ions formed by the α-rays in passing through liquid water.   And this at once leads to fundamental questions affecting the ionisation of liquids which cannot at present be answered.   Thus the whole subject of the nature of ionisation is in a very interesting state, and great advances are foreshadowed, which may have a bearing on chemistry and electrochemical problems.   In particular, it is noteworthy that two of the main ideas, which served almost as a scaffolding on which the existing ionisation theory of gases was largely based during its development, namely, the confident assumption that the charge carried by the gas ion was always the same and equal to the single atomic charge, and secondly that the energy required to produce a pair of ions was independent of the nature of the gas, appear (in the light of fuller knowledge) not to have been warranted.

Ionisation ranges of α rays.   Steady progress has been made in the determination of the ionisation ranges of the α rays of other substances than radium by numerous investigators, following the methods of Bragg and Kleeman.   McClung[3] investigated in this way the α-radiation of radium *C* by itself and found it homogeneous, as was to be expected from the original curves of Bragg and Kleeman.   The same homogeneity has been found independently by many investigators in the case of the radiation from polonium or radium *F*.   Kleeman[4] found a

[1] Compare *Ann. Report*, 1905, 298.

[2] *Radioactive Transformations*, 252.   (Constable & Co., 1906.)

[3] *Phil. Mag.*, 1906, [vi], 11, 131.

[4] *Ibid.*, 12, 273.

range in air of 3·8 cm. at 77·34 cm. of mercury pressure.   Levin [1] found 3 86 cm. at 76 cm., and Kučera and Mašek 4·1 cm. at 73·3 cm.   The results of the latter investigators [2] are the most complete They showed that the range of the rays is not affected by the decay of the activity of the polonium with time ; the number of rays expelled grows less, but the character of the individual particle expelled remains the same. Absorption of the rays of polonium by metal films and gases confirmed the square-root law of Bragg and Kleeman.   Lastly, they state that it is not possible to observe any secondary radiation from the α-rays where they impinge, and the effects previously ascribed to this are probably due to the scattering of the original beam, which increases with the atomic weight of the metal acted on.   This agrees with the conclusion of Kleeman (p. 338).   On the other hand, Edgar Meyer,[3] investigating the nature of the absorption of the α-rays of polonium by metals, concludes that neither secondary radiation nor scattering are necessary to explain the results.   The main fact in question is that if two screens of different metals, as aluminium and tin, are used to absorb the rays, the extent of absorption is different according to the order in which the screens are traversed by the rays.[4] It would appear that all that is necessary to explain these and similar results is to suppose that the absorption like ionisation in gases increases as the velocity of the α-particle decreases.   On this view, the effect of superimposing various screens in different ways can be calculated, and the results given agree closely with experiment.   Further discussion must be held over.

In apparent contradiction to the above conclusions that the α-rays produce no secondary radiation by impact is a research of W. H. Logeman,[5] who has proved in a very neat manner the existence of a secondary radiation from a metal plate in a vacuum bombarded by the α-rays of polonium.   The contradiction is but apparent, for the secondary rays in question are so feeble in penetrating power that they could only be observed by working in a vacuum, and consist of the slow-moving electrons or δ-rays discovered by J. J. Thomson.   With no electric field acting, a plate of polonium gives out to an opposed plate more − than + electricity, but by the application of an electric field in the right direction the emission of negative electricity from the polonium plate can be suppressed, so that the + emission predominates. If, however, a suitable magnetic field is employed to deviate the negative charges and to return them to their origin, the + emission is only one-fifth of that when the electric field is employed.   The explanation is that the plate bombarded gives out slow-moving

[1] *Phys. Zeit.*, 1906, **7**, 519 ; *Amer. J. Sci.*, 1906, **22**, 8.

[2] *Phys. Zeit.*, 1906, **7**, 337, 631 and 650.   [3] *Ibid.*, 917.

[4] Mme. Curie, *Thesis* reprinted from the *Chemical News*, p. 56.

[5] *Proc. Roy. Soc.*, 1906, **78** *A*, 212.

negative charges no less than the polonium plate, and these also are readily returned to their origin by the magnetic field.   The electric field, on the other hand, which suppresses the negative charges from the polonium, carries those from the bombarded plate to the polonium plate, and the effect is added to the positive current conveyed by the α-particles from the polonium to the bombarded plate.   The positive current then appears to be much greater than when a magnetic field is acting.

Returning to the subject of ionisation ranges, Hahn [1] has applied the method with fruitful and novel results to the α-rays of actinium and thorium.   This has been rendered possible by the separation from these elements of intensely active new disintegration products, radioactinium and radiothorium, some account of which follows later (p. 363).   Only very intensely active preparations are suitable for the determination of ionisation ranges, and the extension of the results to thorium, as also the case of Rutherford and Hahn's measurement of the constants of the α rays from this element already described, exemplifies the very valuable results that have followed the separation of radiothorium. Both radiothorium and radioactinium are considered to be the *first* product of the parent element, the initial change of which is in each case rayless, so that these preparations exhibit in intensified degree *the whole* of the characteristic radioactivity of the parent elements. The excited activity of thorium was first investigated.   Hitherto it has been supposed that the rays in this case come solely from thorium *B*, as thorium *A*, the first product deposited from the thorium emanation, undergoes an apparently rayless change (see, however, p. 348). It was at once seen that the curve connecting ionisation with distance was not due to a homogeneous type of α-radiation, but to two types of different ranges superimposed.   The ranges in air were 8·6 cm. and 5·0 cm.   Sufficient grounds are furnished in the paper for the conclusion that the radiation of thorium *B* is derived from two successive products, called thorium *B* and thorium *C*, both of which give out α rays on disintegration, but it is not yet possible to say which change gives the more penetrating and which the less penetrating type.   From analogy to radium it is provisionally concluded that the thorium *C* gives the more penetrating type and also the *β* and *γ* rays.   According to the evidence, the change of thorium *B* into thorium *C* must be extremely rapid, for the two types occur together in all circumstances in unchanged relative amount, and for this reason no actual separation has been effected.   The new type of α rays here disclosed must not be confounded with yet another new type found this year from thorium *A* by von Lerch (p. 348).

The curve in the case of the α radiation of radiothorium itself, freed

[1] *Phil. Mag.*, 1906, [vi], **11**, 792 ; **12**, 82.

from succeeding products, proved to be simple, the rays having a range of approximately 3·9 cm. The curve for thorium X freed from the later products disclosed also a homogeneous α-radiation of range 5·7 cm. The range of the rays from the thorium emanation was estimated by a special scintillation method to be about 5·5 cm. Thus the whole of the ranges of the five types of α-rays emitted by thorium have been determined, and it is interesting that the range is on the average higher and the velocity therefore greater than in the case of radium. Indeed, the α-particle of range 8·6 cm. from thorium C is the fastest moving α-particle known. A beautiful photograph showing the lesser deviation suffered by this particle in comparison with that from radium C, the swiftest particle from radium, is to be found in Rutherford and Hahn's paper on the mass and velocity of the α-particles from thorium already referred to. On the clear view afforded by the disintegration theory, it is of course a matter of no comment that a feebly active body like thorium should emit an α-particle with greater velocity and energy than in the case of an intensely active body like radium, but no more striking example could be deduced of the independence of the rate of atomic disintegration, not only on its external environment, but also on the quantity of internal energy liberated in the process.

Some observations of Lise Meitner[1] on the α-rays of thorium B resulted in the confirmation of the square-root law of absorption of Bragg. In the case of the β-rays the absorption does not follow the square-root law, but increases with, although slower than, the specific gravity of the metal.

For actinium, Hahn[2] gives the following ranges for the four types of α-radiation : radio-actinium, 4·8 cm.; actinium X, 6·55 cm.; actinium emanation, 5·8 cm. ; actinium B, 5·50 cm. In the relative magnitude of the ranges of the rays of the successive products the actinium series bears a close resemblance to that of thorium, a resemblance which is extending itself to all the radioactive properties of the two substances. The various α-rays from actinium are the most nearly alike in range, those from thorium exhibit the greatest diversity, whilst those from radium occupy an intermediate position. The α-radiation from the excited activity of actinium (actinium B), unlike that from thorium, is completely homogeneous.

The researches of H. Willy Schmidt,[3] remarkable in many directions discussed later, have resulted incidentally in settling the question left open from Bragg and Kleeman's work[4] of the respective ranges of the α-rays from radium A and the radium emanation. Schmidt has

[1] *Phys. Zeit.*, 1906, **7**, 588.   [2] *Phil. Mag.*, 1906, [vi], **12**, 244.
[3] *Phys. Zeit.*, 1905, **6**, 897 ; 1906, **7**, 764 ; *Ann. Physik.*, 1906, [iv], **21**, 609.
[4] *Ann. Report* 1905, 296.

shown that the less penetrating of the two types of α-radiation present in the radiation from the active deposit immediately after its formation from the radium emanation, and which is due to radium A, has a range greater than 4·5 cm. and less than 5·1 cm., so that the range of 4·83 cm. measured by Bragg must be ascribed to the rays from radium A, and that of 4·23 cm. to the rays from the radium emanation.

For use in cases of feebly radioactive bodies where a direct determination of the range of the α-radiation is impossible, Bragg[1] has derived an indirect method which he has applied to the determination of the ranges of the α-rays from uranium and thorium. Bragg obtains mathematically an expression connecting ionisation current due to α-rays, from layers of radioactive matter of various depths covered with uniform sheets of metal of various thickness and known stopping power, with the range of the α-ray in question, in such a way that the range can be deduced from measurement of the ionisation current under various conditions. In this way it is shown that the initial α-ray expelled from both thorium and uranium has the same range as that of the initial α-ray expelled from radium, namely, about 3·5 cm. This is in fair agreement with the direct measurement of Hahn for thorium (radiothorium), which gave 3·9 cm. (p. 342). From the relative ionisation produced from similar quantities of uranium and thorium preparations, and the number of α-ray changes in each case contributing to the activity, Bragg has deduced the relative rates of change of these two elements to be in the ratio of 5 to 1. Uranium and thorium are of very similar α-activity, but since there are five successive changes contributing α rays in thorium and only one in uranium, the uranium must be disintegrating much the more rapidly. The actual ratio of Bragg is, however, vitiated, as Rutherford has pointed out, by the subsequent work of Dadourian and Boltwood (p. 362), who has shown that commercial thorium preparations do not contain their full amount of radiothorium, about half being apparently separated during the process of manufacture. To get the true ratio, which is probably about 5 to 2, the measurements must be repeated with some thorium mineral, such as thorianite, containing a known percentage of thorium in equilibrium with its disintegration products.

Positive Charge carried by the α Particle. The difficult question as to whether the α-particle is charged at the moment of its expulsion from the parent atom[2] has this year been experimentally attacked by Ewers[3] and Soddy.[4] Ewers investigated the α rays of polonium in the highest vacuum he could produce, and obtained no difference in the value of the charge carried by the α rays on account of the high vacuum. He concluded against the hypothesis that the α particle was uncharged

[1] *Phil. Mag.*, 1906, [vi], 11, 754.   [2] Compare *Ann. Report*, 1905, 362.

[3] *Phys. Zeit.*, 1906, 7, 118.   [4] *Nature*, Aug. 2nd, 1906, p. 316.

at the moment of its expulsion frnm the parent atom. He also measured the constants of the slow-velocity electrons (δ-rays) accompanying the α-radiation, and found for e/m $1\cdot48 \times 10^7$ and for v $3\cdot25 \times 10^8$, which, however, are not in agreement with the experiments of Logeman (p. 341). It has been pointed out by Bragg [1] and Soddy [2] that the experiments of Ewers do not suffice to answer the question as to the initial state of the α-particle on expulsion, for in his experiments the α-particles must first pass through the thickness of the radioactive layer of polonium, and must, therefore, become charged before emerging into the vacuum. The conditions to be realised are, according to Soddy, not only a vacuum so high that no gas molecule is encountered by the α-particle in its path, but also a layer of radioactive matter as the source of α-rays, not exceeding one molecule in thickness. This was attempted experimentally by using radium C as the source of α-rays, the deposit being produced inside, and confined within a certain length of, thermometer tubing of the smallest possible bore, from one of the open ends of which a narrow pencil of α-rays emerged. Under the action of a magnetic field the rays are readily deviated, and none escapes the narrow tube. After many failures, it was found in three consecutive experiments that a magnetic field which completely deviated the beam in a low vacuum no longer affected it in the highest possible vacuum, and it was concluded that the α-particle was uncharged on expulsion. Only a preliminary account of this work has so far appeared.

The Disintegration Series radium A, radium B, radium C.—This series has hitherto presented some anomalies and unexplained divergences from the requirements of the simple theory, which have received during the year exhaustive and critical examination, resulting in the complete vindication of the theory in its original form. Rutherford concluded [3] that his experimental results would agree more closely with theory if radium A and radium B were regarded as simultaneous rather than as successive products of the radium emanation, but that further work was required before so fundamental a conclusion could be accepted. A similar idea has been proposed by him [4] to account for the position of actinium in the uranium-radium series, which is also anomalous. However, new results have, so far at least as the radium series is concerned, dispensed with the necessity of the above assumption. The conclusion of Bronson [5] that radium B has a longer period of change than radium C, instead of the contrary as previously assumed, and that both periods must be reduced, has also been arrived at independently by H. W. Schmidt

[1] *Phys. Zeit.*, 1906, **7**, 452.   [2] *Loc. cit.*

[3] Compare *Radioactive Transformations*, p. 115.   [4] *Ibid.*, p. 177.

[5] *Phil. Mag.*, 1906, [vi], **11**, 143; *Ann. Report*, 1905, 307.

and by von Lerch. The latter[1] arrived at his conclusions by the electrochemical separation of the two products radium B and radium C, the former of which has been regarded as rayless, but as producing radium C, which then gives all three kinds of rays. Radium C behaves as electrochemically " nobler " than radium B, and by immersing a copper or nickel plate in the solution of the active deposit, or by electrolysis with small current density using a polished platinum cathode, only the radium C is deposited. In the same way, thorium B ($+$ thorium C) is separated from thorium A, hitherto regarded as rayless.[2] If barium is precipitated as sulphate in the solution, the radium C remains in solution while the radium B is carried down with the precipitate. Copper precipitated with caustic potash leaves some of the radium B in solution, the remainder, together with the radium C, being precipitated. The radium C, whether separated as in Bronson's methods by volatilisation of the radium B, or by the new methods of von Lerch, has the quicker period.

H. W. Schmidt,[3] in addition to showing that the decay curves could be better explained by supposing that radium C possessed the quicker period, has shown that the change of radium B into radium C is not altogether rayless, as previously assumed, but that β-rays of a type unusually feeble in penetrating power are emitted, and with these two additions the experimental results agree perfectly with the theory without further assumptions. The same discovery of the emission of β-rays from radium B has been made independently by W. Duane[4] and by Gruner,[5] the latter in a mathematical contribution to the theory of radioactive change, from a study of the experimental results of Curie and Danne. Schmidt investigated the decay curves of the active deposit on a wire, immediately after short exposure to the radium emanation, through metal screens of successively increasing thickness. 0·03 mm. of aluminium cuts off all the α-rays from radium A, and the decay curve, instead of showing the sharp initial decay characteristic of the change of radium A, rises to a maximum steadily in thirty minutes. With increasing thickness of aluminium the maximum is reached sooner, and with 0·068 mm. in eleven minutes. Screens, successively added, of 0·1, 0·2, and 0·4 mm. caused the period of maximum again to increase until it reached thirty-five minutes. The only explanation is that radium B gives out rays somewhat more penetrating than α-rays and less penetrating than the common β rays.

In a further examination, the methods of von Lerch in separating radium B and radium C were employed, and it was found that the β rays of radium B could be deviated by a magnetic field, and more

[1] *Wien. Sitzungsber.*, 1906, **115**, Abt. IIa, 197 ; *Ann. Physik.*, 1905, [iv], **20**, 345.

[2] *Ibid.*, March, 1905.   [3] *Loc. cit.*, p. 343.

[4] *Science*, 1906, **24**, 48.   [5] *Ann. Physik.*, 1906, [iv], **19**, 160.

readily, so that they must travel at a lower velocity than those of radium C. Duane has shown that they carry negative charges. The periods[1] of the three products may be taken as follows : radium A, three minutes ; radium B, twenty-six minutes ; radium C, nineteen minutes; and the theoretical curves calculated from these periods now agree far better with the experimental than if it is supposed that radium A and radium B are simultaneous products.

Bronson,[2] in a special research, examined the radiation of radium B to see if a-rays, possibly of very slight penetrating power, were also given out, but with a negative result.

Another question remains for consideration in connexion with this disintegration series. Curie and Danne had explained their experimental results originally on the view that the rate of transformation in this series is affected by high temperature, and the effect of submitting the active deposit to a high temperature has been examined both by Bronson and Makower with contradictory results. The former[3] maintains that there is no alteration of the rate of change. Wires made active in the radium emanation were afterwards sealed into tubes of hard glass, so that none of the radioactive matter could escape by volatilisation, and were heated, it is stated, up to temperatures of at least 1100°. It is difficult, however, to believe that such high temperatures can be attained with glass tubes. Makower,[4] working at much higher temperatures in vessels of sealed quartz, investigated the effect of heating on the external radiation from the excited activity inside the vessel. The rays in question are the β- and γ-rays derived from radium C and not from the emanation. The activity measured immediately after the tube had been heated for fifteen minutes to a temperature between the melting points of platinum and of nickel was found to have fallen about 15 per cent., but in the course of an hour recovered its original value. This was repeated five times for the same tube with similar results, and in a second experiment at lower temperatures (1000° to 1200°) it was found that while heating for ten minutes had little effect, heating for one hour produced a temporary lowering of activity of from 4 to 9 per cent., while longer heating produced no further effect. In a further paper to the Royal Society just published, Bronson[5] has maintained his original conclusion, and states that there is no alteration in the constants between − 180° and 1600°, so that the question therefore remains unsettled.

[1] By "period" used as above without further qualification is now commonly understood the period of half-transformation. Multiplying this by 1·45 gives the "average life" which is the time required for the quantity to be reduced to ε^{-1} (0·368) of the initial. The reciprocal of the average life is the "radioactive constant" λ.

[2] *Phil. Mag.*, 1906, [vi], **11**, 810.

[3] *Ibid.*, 142.

[4] *Proc. Roy. Soc.*, 1906, **77** A, 241.

[5] *Ibid.*, 1907, **78**, A, 494.

Other α-Radiations previously overlooked.—Closely connected with the preceding results are two researches which have resulted in the discovery of radiations previously overlooked in other disintegrations. Von Lerch [1] has concluded that thorium *A*, hitherto regarded as rayless, emits a small amount of ionising radiation, in part less penetrating, but chiefly more penetrating in character than the α-rays emitted by thorium *B* (+ thorium *C*).   Thorium *B* was separated electrochemically from thorium *A*, and the radiation of the former compared with that of the unseparated activity using various thicknesses of absorbing screens.   The close agreement between the decay curves and theory on the earlier assumption that the change of thorium *A* is rayless, shows that the amount of radiation from this body must be relatively small.

Moore and Schlundt,[2] in an investigation of new methods of separation of uranium *X* from uranium, have made the observation that the radiation of uranium *X* is not entirely due to β rays, as before thought, but that there is a small amount of a feebly penetrating radiation also, which they ascribe without sufficient proof to α rays. Hitherto, although it has been noticed that uranium *X* has a feeble non-penetrating radiation, this has been attributed to a trace of uranium not completely separated.   Moore and Schlundt, however, show that this cannot be the case, for the two types of radiation both decay, and at the same rate.   A more thorough examination of this radiation is much to be desired, for the results of the authors give no clue to the real nature of the radiation, whether it is an α-radiation as they assume, or a feebly penetrating β-radiation of the type given by radium *B*. The new methods of separation referred to consist in dissolving uranyl nitrate in various solvents, acetone, various alcohols, methyl and ethyl acetate, &c., stirring in a little freshly precipitated ferric hydroxide, and filtering.   The filtrate containing the uranium is found to be quite free from uranium *X*, which remains with the precipitate. Another case of a feeble radiation previously overlooked is considered under actinium (p. 363).

β Rays.—Important advances have also been made in our knowledge of the β-rays, and a beginning, perhaps, made in a theory of the mechanism of their absorption by matter, which is so markedly different in nature from that shown by Bragg for the α rays.

It has always been suspected without actual proof that in thorium, as in radium, the β rays result only in the last change, but until now the difficulty of separating thorium *X* from the later products, giving β rays, has prevented a definite answer to the question.   Levin [3] has investigated from this point of view both thorium and actinium,

[1] *Phys. Zeit.*, 1906, **7**, 913.   [2] *Phil. Mag.*, 1906, [vi], **12**, 393.
[3] *Ibid.*, 177.

and has concluded that the only members of the series producing β-rays are in each case the last, thorium B (+ thorium C) and actinium B. Thorium X carefully separated from later products of change possesses only two or three per cent. of the β-activity ultimately attained, and actinium X is similar.

A very complete examination of the absorption of the β-rays of uranium has been made by J. A. Crowther.[1] As Rutherford has shown, this radiation is fairly homogeneous, and absorbed according to an exponential law, $I/I_0 = e^{-\lambda d}$, where I is the intensity of the radiation, initially of intensity I_0, after passage through a thickness d of material. λ is the coefficient of absorption. This coefficient is not proportional to the density (ρ), and λ/ρ varies from 5·7 for glass, mica, wood, iron, and aluminium to 13·2 for tin, whereas Lenard found for the cathode rays of the Crookes tube that the absorption was strictly proportional to density (Lenard's density law). Godlewski has shown that the β-rays of actinium are also homogeneous and absorbed exponentially, while here the variations from the density law are smaller. Crowther has determined λ/ρ for thirty elements, and finds that the latter arrange themselves in groups according to the groups of the periodic table when the value of λ/ρ is plotted against the atomic weight. In compounds the absorption is strictly additive, and the secondary radiation set up by the β-rays of uranium is much less than that produced by the β-rays of radium.

H. W. Schmidt[2] has investigated the β-radiation of radium (derived from radium B and radium C), and made the remarkable observation that within certain screen thicknesses the absorption of both types proceeds according to an exponential law. In this way he analysed the β-radiation into five homogeneous types, three derived from radium B and two from radium C. For the former the respective thicknesses of aluminium required for half absorption are 0·0078, 0·087, and 0·53 mm., for the latter 0·131 and 0·53 mm. He points out that it is doubtful if such an analysis can have a real physical meaning, but if so, it seems to open the way to a clearer view of the mechanism of absorption. It seems possible, if the absorption of β-rays follows an exponential law, that the β-particle passes through the atoms of matter completely unchecked until it is suddenly and completely stopped. This view accords with Kaufmann's work that the velocity of the β-particles which escape an absorbing screen are not retarded during their passage through the screen, and with Kleeman's observation that ionisation produced by β-rays after passage through a thick aluminium plate shows little tendency to initial recombination.

Secondary Radiation of β-Rays.—This view accounts well also for the

[1] *Phil. Mag.*, 1906, [vi], **12**, 379.

[2] *Phys. Zeit.*, 1906, **7**, 764 ; *Ann. Physik.*, 1906, [iv], **21**, 609.

fact observed by McClelland, and recently examined by S. J. Allen,[1] that the velocity and the penetrating power of the electrons constituting the secondary radiation set up by impact of the β-rays is not greatly, if at all, less than for the primary rays themselves, for the "stopping" of the primary rays may well consist in their being turned through a large arc, as a comet at perihelion, to reappear as secondary rays at the bombarded surface. S. J. Allen repeated and confirmed by an electrical method the work of Kaufmann, and found also that the ratio e/m of the secondary radiation, like that of the primary, increases with the velocity of the secondary ray. McClelland[2] and McClelland and Hackett,[3] in continuation of their investigations on secondary radiation, found that the energy of the secondary radiation from a plate of lead, for example, was equal to one half of the energy of the primary rays. The ratio diminished with the atomic weight of the metal, being lowest for carbon and next lowest, but still above 20 per cent., for sodium, aluminium, and magnesium. The secondary radiation of compounds is an additive function of the component elements, and can be calculated from the radiating power of the constituents. The important influence of secondary radiation on the apparent coefficient of absorption of the primary rays is pointed out, and it is stated that owing to successive generation of fresh β-particles as secondary rays the apparent distance penetrated by the primary rays is much increased.

K. Seigl[4] showed that the secondary radiation produced on impact by the β-rays of radium is capable of exciting strong fluorescence in barium platinocyanide. It was weakest for aluminium and strongest for lead, increasing with the atomic weight of the metal, as McClelland has shown. Using tinfoil, it was found that the effect increased with successive numbers of layers of foil up to 50 layers.

The Electronic Theory of Matter.—It may be stated without fear of contradiction that the theory that the atom is made up entirely or to any substantial extent of electrons is now generally regarded as being very much open to question. From spectroscopic and other evidence it is certain that electrons are universal constituents of atoms, but for the further very sweeping deduction that the atoms are composed of electrons there never has been much positive evidence in the past, whilst against the view some definite experimental evidence can now be urged. It is interesting to note that Prof. J. J. Thomson, to whom the electronic theory of matter is largely due, has himself this year brought forward considerations which have practically made the theory untenable. The view that the β-ray electrons do not in their passage through matter diminish continuously in speed, but proceed more or less unaffected

[1] *Phys. Review*, 1906, **22**, 375.   [2] *Trans. Roy. Dubl. Soc.*, 1906, ii, **9**, 9.

[3] *Ibid.*, p. 27.   [4] *Phys. Zeit.*, 1906, **7**, 106.

until they are suddenly stopped or turned through a large angle to reappear as secondary radiation, bears upon the present question. Considering the enormous number of atoms a β-ray electron can penetrate without being greatly affected, and the certainty that the approach of the radiant electron to an electron in an atom must result in deviation or loss of velocity of the former, it becomes extremely difficult to believe in the reality of the view that the atom is substantially constituted of swarms of electrons in regular motion. The penetrating power of the β-ray electron was one of three methods developed by J. J. Thomson[1] to determine the number of electrons in an atom, each of which led to the result, the importance of which cannot be overestimated, that the number of electrons in any atom is of the same order as, and probably equal to, the atomic weight in terms of hydrogen as unity, a conclusion which practically leaves the whole problem of the ultimate constitution of matter where it was, and which is in sharp conflict with the electronic theory of matter, which assumed a number of electrons a thousand times greater. The two other methods of attacking the question depended, the one on the scattering of Röntgen rays by gases, for which the work of Barkla on the ratio of the energy scattered to that in the primary radiation furnished the required data, and the other on the dispersion of light by gases. In the latter method a light wave is considered crossing the atom and subjecting it to the action of the electric field in the wave-front for a period the longer the longer the wave-length of the light. This field affects the displacement of the positively and negatively charged parts of the atom in opposite directions, polarising the atom and increasing the refractive index of the medium. This polarisation and increase of refractive index will in general be the greater the longer the wave-length causing dispersion, and the amount depends upon the relative masses of the positive and negative parts of the atom. For the mathematical development of these three methods the original paper must be consulted. The result that all but about one thousandth of the mass is associated with the positive part of the atom shows that an altogether exaggerated *rôle* has been attached to the electron in the constitution of matter.

A paper with revolutionary theoretical conclusions, which, however must await further confirmation before being accepted, has been published by H. A. Bumstead[2] on the heating effects produced by Röntgen rays in different metals. He found that the absorption of equal amounts of Röntgen radiation in lead and in zinc produced approximately double as much heat in the lead as in the zinc. A somewhat complicated method of measurement was employed, depending on a radiometer effect of the heated metal. The hypothesis is suggested

[1] *Phil. Mag.*, 1906, [vi], 11, 769.   [2] *Ibid.*, 292.

that by means of Röntgen rays the atoms of certain elements may be artificially broken up and the internal energy liberated, causing the excess of the heating effect observed, but such a fundamental conclusion can only be accepted after the most rigorous and exhaustive examination.

γ-Rays.—J. J. Thomson [1] has proved that the effects ascribed by Paschen to the γ-rays carrying negative charges are due to secondary radiation set up by the γ-rays, and that the latter do not carry charges. The same author has shown [2] that prolonged action of the γ-rays on metals does not cause induced radioactivity, and Bumstead has shown [3] that even when arrangements are made to detect an extremely short-lived radioactivity, a negative result is also obtained.

Schmidt found no appreciable γ-radiation accompanying the new β-radiation of radium *B*. Stefan Meyer and von Schweidler [4] found similarly for radium *E*, the β-ray constituent of radio-lead, that there was no appreciable γ-radiation accompanying the β rays. If they exist their effect is less than 0·03 per cent. of the β-rays. The same conclusion was indirectly drawn by Eve,[5] and may be inferred from a paper by Giesel [6] on "β-Polonium," which, however, there is no doubt owes its β-activity to the presence of radium *E*.

Eve showed that the γ-radiation of uranium and actinium is more readily absorbed than that from radium and thorium, so that by the use of a screen consisting of 1 cm. thickness of lead, the effect of the former may be eliminated, and the rays penetrating such a screen used as a measure of the amount of radium and thorium, for example, in a mineral, without the necessity of powdering it or dissolving it, or even removing it from its containing vessel. On comparing the γ-activity of a kilogram of uraninite from Joachimsthal, which contains all the disintegration products of radium, including radium *E*, in radio active equilibrium, with that from a known amount of pure radium bromide, which contains no appreciable amount of radium *E*, it was concluded that radium *E* either does not give γ-rays, or more probably that its γ-radiation is, like that of uranium, easily absorbed. However, Meyer and von Schweidler have proved that no γ-rays are emitted. Eve's research had an interesting sequel.   Even assuming that the radium *E* give no γ-rays itself, the amount of γ-radiation from the mineral was low, so that the quantity of radium contained in it could only be one half of that to be expected from the work of Rutherford and Boltwood,[7] who found 0·72 gram radium per ton of uranium.   This

[1] *Proc. Camb. Phil. Soc.*, 1905, **13**, 121.   [2] *Ibid.*, p. 124.   [3] *Ibid.*, p. 125.
[4] *Wien. Anzeiger*, 1906, 12 ; *Sitzung*, April 26th, 1906.
[5] *Phil. Mag.*, 1906, [vi], **11**, 586 ; *Amer. J. Sci.*, 1906, **22**, 4.
[6] *Ber.*, 1906, **39**, 780.   [7] *Ann. Report*, 1905, 310.

led these investigators to redetermine this constant, [1] with the result that an error was discovered. It was found that about one half of the radium in the standard solution had precipitated on standing without having been noticed. A redetermination gave the value 0·38 gram per ton, a number agreeing with Eve's measurements by means of the γ-radiation, and more nearly what is actually extracted in practice. A later paper by Eve on the relative γ-activity of radium and thorium is considered in the section on radio-thorium (p. 362), and one on the γ-radiation from the earth's surface in the section on radioactive minerals (p. 359).

Action of Ultra-violet Light on Different Metals.—Sir William Ramsay and J. F. Spencer [2] have investigated the effect of ultra-violet light on a large number of metals and compounds. It is well known that when certain metals, particularly zinc and the alkali metals, are illuminated by ultra-violet light, electrons are expelled from the metal surface, which, if negatively charged, is rapidly discharged by the light. It was found that the order in which the metals arrange themselves in their action under ultra-violet light is the same as in the case of their electro-potentials, exceptions being noticed in the case of those elements, as iron, chromium, nickel, and cobalt, which readily assume the passive form. The compounds examined, sulphides and iodides of the metals, discharged negative electricity like the metals, only more slowly. An examination was also made of the "tiring" of magnesium, zinc, tin, and aluminium exposed to ultra-violet light, the rate of discharge becoming slower with prolonged action. They found on plotting rates of discharge against the times of exposure that the curves showed a number of breaks corresponding with the number of valencies of the metals, except for aluminium, which showed at least five or six breaks. The authors interpret their results on the view that atoms and electrons may be associated in three ways: (1) as in an ion in electrolysis; (2) as in an electrostatically charged object, where the electricity is confined to the surface and may be likened to the wetting of a solid by a liquid; and (3) in a more intimate manner, in such a way that the loss of an electron or electrons is attended by actual transmutation of the original element without the appearance of a positive charge.

The "tiring" of metals under the action of ultra-violet light has also been investigated by H. S. Allen,[3] who finds the process can be represented as the sum of two exponentials, as in the case of two successive radioactive changes, and the author suggests that the metal suffers by the process successive transformation into two new modifications, but leaves open for further examination the question of the

[1] *Amer. J. Sci.*, 1906, **22**, 1.   [2] *Phil. Mag.*, 1906, [vi], **12**, 397.
[3] *Proc. Roy. Soc.*, 1907, **78**, *A*, 483.

nature of the latter and the precise nature of the changes.   These results are too recently published for full consideration.

General Properties of Radiations.—Rutherford [1] shows that the distribution of the intensity of radiation in space from a surface coated superficially, as for example in the case of radium C, with a radioactive substance is totally different from what would obtain in the case of a similar surface emitting light or heat.   In the latter case the intensity varies with the cosine of the angle between the normal to the surface and the direction of the emitted ray, according to what is known as Lambert's law, and usually explained by supposing that the light comes from a sensible depth below the surface.   In the case considered the radiation is strictly superficial, and there is no cosine law. Many beautiful and striking photographs of the effects obtained in consequence are given in the paper.   In a paper entitled "Fluorescence and Lambert's Law," R. W. Wood [2] has imitated Rutherford's effect for radioactive substances with a surface coated with a thin layer of phosphorescent substance, by allowing, for example, a fine dust of Balmain's luminous paint suspended in air to deposit on the surface.

The glow from an uncovered radium preparation in air has been further examined by Sir William and Lady Huggins, [3] and by Walter. [4]   The phosphorescent glow extends about 2 cm. in air when examined photographically, and shows the nitrogen bands.   The rays from polonium possess the same property, and Walter [5] has made the interesting observation that the spectrum in the case of radium most resembles the band spectrum of the blue cathode light, whilst that of polonium resembles the red positive glow of a nitrogen vacuum tube. Stark [6] has shown that the glow in the case of polonium is not affected by an electric field, and argues that the molecules emitting the light are not charged electrically.

A. Miethe [7] has investigated the action of radium rays, presumably the β- and γ-rays, on a large number of gems, and finds that many show coloration, whereas in the case of those brightly coloured originally the colour is readily changed.   A colourless diamond from Brazil showed no coloration after long exposure, but a Borneo stone, originally colourless, turned bright citron-yellow in sixteen days, the colour being only partially discharged on heating to redness. [8]   A bright blue sapphire (corundum) from Ceylon showed a very remarkable series of colour changes under similar treatment, passing through green and bright

[1] *Phil. Mag.*, 1906, [vi], **11**, 152.
[2] *Ibid.*, 783.
[3] *Proc. Roy. Soc.*, 1906, **78** *A*, 212.
[4] *Ann. Physik.*, 1905, [iv], **19**, 1030.
[5] *Ibid.*, 1906, **20**, 327.
[6] *Phys. Zeit.*, 1906, **7**, 892.
[7] *Ann. Physik.*, 1906, [iv], **19**, 633.
[8] Compare C. W. R., *Nature*, July 19 1906 p. 271.

yellow to a reddish-gold yellow, which was discharged on heating, but returned to some extent when the stone cooled. Ruby, Ceylon chrysoberyl, blue topaz, and Brazilian amethyst showed no change, whilst a colourless quartz rock-crystal turned blue-grey very slowly. Two crystals of Brazilian tourmaline, each colourless at the one end and the one rose-coloured the other bright green at the other end, showed, when the colourless ends were exposed to radium rays, each the same bright coloration as that of the other end of the crystal.

Jorissen and Ringer [1] investigated the action of β-rays of radium on a mixture of hydrogen and chlorine, and found a slow combination, about half a c.c. combining in ninety-six hours. With hydrogen and oxygen there was no combination, and the work of B. Davis and C. W. Edwards,[2] who found a rapid combination when the radium salt was actually placed in the gas probably due to the action of the α-rays in the latter case and may, indeed, be connected with the known large heating effect of the α-rays. Sir W. Ramsay has shown that the β-rays do not decompose liquid water. F. Kohlrausch [3] found no sudden change in the conductivity of water when traversed by β-rays of radium, but after prolonged action of the rays the conductivity very slightly increased. Kohlrausch and F. Henning [4] found that solutions of radium bromide behave as completely normal so far as their conductivity is concerned, and no peculiar behaviour due to the presence of the radium was observed.

General Properties of Radium.—The energy carried away by the penetrating radiations of radium has been the subject of an investigation by Precht,[5] who finds that the heat evolved, measured in a Bunsen's ice-calorimeter, is increased 10 per cent. when the radium preparation is surrounded by 3 mm. of lead, but is not further increased by increasing the thickness of lead. Obviously some of the β-radiation must be absorbed in the calorimeter itself even with unscreened radium inside, so that the 10 per cent. difference must be for a part only of the energy of the β-rays. The actual heat evolution calculated for 1 gram of the element radium was $122 \cdot 2$ calories per hour unscreened and $134 \cdot 4$ screened. These are considerably higher than the usually accepted values. These experiments recall those of Bumstead with X-rays on metals (p. 351), and may be found to be closely connected with them.

The sample of 25 mg. of anhydrous radium bromide used by Precht in these experiments was sealed in a glass tube 2 mm. in bore and $0 \cdot 5$ mm. wall thickness, and about eleven months after sealing exploded violently.[6] Precht ascribed the explosion to the generation of suffi-

[1] *Ber.*, 1906, **39**, 2093.
[2] *J. Soc. Chem. Ind.*, 1905, **24**, 266.
[3] *Ann. Physik.*, 1906, [iv], **20**, 87.
[4] *Ibid.*, p. 96.
[5] *Ibid.*, 1906, **21**, 595.
[6] *Phys. Zeit.*, 1906, **7**, 33.

cient gas (helium and emanation) to burst the tube, which, however, would probably require 20 atmospheres pressure.   Mercanton [1] found no excess of pressure in a glass tube containing 15 mg. radium bromide after it had been kept sealed for more than three years, and this is to be expected from the common view that the effect is due to electrical strain, as the amount of gas generated from an anhydrous salt is for practical purposes negligible even after long periods.   Mercanton also showed that radium emanation does not diffuse at all through glass heated to its softening point.   Rutherford has found [2] that charcoal at the ordinary temperature possesses the property of absorbing the radium emanation completely, so that the escape of the latter from an open vessel containing radium may be entirely prevented if the exit tube is filled with charcoal.   Loewenthal [3] has investigated the physiological action of the radium emanation dissolved in water and injected into the system.   There does not appear to be any injurious effect on healthy subjects, but with patients suffering from chronic rheumatism and similar infirmities there occurs a constant reaction after the treatment, accompanied by inflammation and swelling of the joints, which resembles closely the reaction induced by certain healing springs.   The same effect can be produced by inhaling the emanation.

W. A. Douglas Rudge [4] showed that the action of radium on sterilised gelatin, first noticed by Butler Burke, is exhibited by salts of barium and other metals producing an insoluble sulphate, and is due to the precipitation of the sulphate of the metal by sulphuric acid present in the gelatin.   Purification of the gelatin from sulphate stops the action, which can be started again by introducing a soluble sulphate. Radium has no specific action on gelatin apart from the barium present, and other radioactive substances not containing barium are also without effect.

Boltwood [5] has investigated the escape of the emanation from thin films of radium salts carefully protected from the action of moisture in a desiccator.   Mme. Curie has stated that the activity of a radium barium preparation increases to five or six times the initial activity after some months.   If first heated to a red heat the maximum ultimately attained is half again as great, while if the preparation is kept fused for two hours the maximum is twice as great.   Boltwood evaporated a solution of radium barium chloride to produce thin films, and observed (1) the minimum or initial activity, (2) the equilibrium or maximum activity attained after the films had been kept some weeks in a desiccator, (3) the

[1] *Phys. Zeit.*, 1906, **7**, 372.   [2] *Nature*, Oct. 25, 1906, p. 635.

[3] *Phys. Zeit.*, 1906, **7**, 563.

[4] *Proc. Camb. Phil. Soc.*, 1906, **13**, 258 ; *Proc. Roy. Soc.*, 1906, **78**, *A*, 350.

[5] *Amer. J. Sci.*, 1906, **21**, 409.

amount of emanation actually present in the film under the last conditions, and (4) the total emanation generated in the same time by a similar amount of radium in solution in a closed flask. In this way it was shown that only about 70 per cent. of the total emanation is retained by the dry film and 30 per cent. escapes into the air. The final activity that would be attained if the whole of the emanation were retained is 5·6 times the initial activity. In the case of a film of pure radium bromide, only 45 per cent. of the emanation was retained. Boltwood points out that the ratio 5·6 to 1 is that of the sum of the ranges of the four a-rays to the range of the a-ray from radium itself, but this is probably a mere coincidence.

Radioactivity of Thermal Springs.—A large number of papers, to which only passing reference can be made here, have appeared on the radioactivity of thermal and other springs, and the occurrence of argon and helium in the gases therefrom. H. W. Schmidt and K. Kurz[1] concluded from an examination of the springs of the Grand Duchy of Hesse that nearly all springs contain a radioactive emanation, generally that of radium, but in some few cases also that of thorium. The amount does not depend at all on the depth, temperature, or chemical quality of the spring, but only on the geological relations, springs from igneous rocks being the most active, whilst those from sedimentary rocks, and especially chalk and sand, are least. The most active springs are some well-known healing springs, but by no means all the latter exhibit strong activity. At Kreuznach there is a trace of a radium salt itself dissolved in the water, as Strutt found for the Bath waters. Further reference to this spring is made by Gehlhoff,[2] and other papers are by Hauser,[3] Ewers,[4] Curie and Laborde,[5] Dienert and Bouquet,[6] Mache and S. Meyer,[7] and Moore and Schlundt.[8]

Radioactive Minerals.—This section usually receives full consideration in the report on Mineralogical Chemistry, and it remains here merely to direct attention to some mineralogical papers by Paul Gaubert on the distribution of uranium at St. Joachimsthal and in Saxony,[9] and to an especially interesting paper by Marckwald[10] on a new uranium mineral from German East Africa, more radioactive even than the Joachimsthal pitchblende. The mineral occurs disseminated through the mica from the quarries of the Uruguru mountains, and is a black, crystalline pitchblende, more or less weathered into a previously unknown mineral consisting almost entirely of the new compound uranyl carbonate, which is yellow and has never been artificially prepared. Marckwald suggests the name "Rutherfordine" for this

[1] *Phys. Zeit.*, 1906, 7, 209.   [2] *Ibid.*, 590.   [3] *Ibid.*, 593.
[4] *Ibid.*, 224.   [5] *Compt. rend.*, 1906, 142, 146.   [6] *Ibid.*, 449.
[7] *1er Congrès pour l'Étude de la Radiologie, etc.*, Brussels.
[8] *Amer. Electrochem. Soc.*, Sept. 1905.
[9] *Le Radium*, 1906, 3, 1, 132 and 167.   [10] *Centr. Min.*, 1906, 24, 761.

new mineral, in honour of the distinguished pioneer in the study of radioactivity. The unaltered mineral mainly consists of U_3O_8 (87·7 per cent.), contains 7·5 per cent. of lead, has a sp. gr. 8·84, and is 20 per cent. more active than the pitchblende of Joachimsthal. The weathered mineral contains no less than 96 per cent. of uranyl carbonate and 1 per cent. of lead, with sp. gr. 4·82 and a radioactivity equal to the original pitchblende. It is greatly to be hoped that such a valuable mineral will be found in large quantities.

. An analysis of the new mineral thorianite has been published by Büchner,[1] together with the proportion in which the activity is distributed among the constituents. The quantity of helium is given as 8·2 c.c. per gram, and the radioactivity of the sample taken for analysis as 83 per cent. of standard uranium oxide.

Strutt[2] has found traces of neon, estimated as about 1/300th part, in the helium from two radioactive minerals, zircon and cyrtolite, both containing zirconia, by using Dewar's process of fractionating the gases with charcoal cooled in liquid air. The same investigator has made an exhaustive series of analyses of twenty-eight minerals of the earth's crust for the quantity of radium present.[3] He found the igneous rocks contained far more radium than the sedimentary. Granite contains $9·56 \times 10^{-12}$ gram of radium per gram of mineral, or $25·2 \times 10^{-12}$ per c.c. of mineral; but these measurements must now all be halved owing to the error previously referred to (p. 353) in the amount of radium in uranium minerals. The amount of radium necessary to maintain the temperature of the earth is calculated by Strutt to be about $1·75 \times 10^{-13}$ gram per c.c., a quantity which is fifty to sixty times less than the average amount in average igneous rocks, and ten times less than the amount in the poorest samples examined. The conclusion which Strutt draws is that the earth can only consist of a crust of igneous rocks some forty-five miles in depth, the interior being entirely free from radium and composed of a totally different material, which is in agreement with the views of Milne drawn from the study of seismological phenomena. This conclusion has been the source of much discussion, and many other explanations have been advanced. One of these, supported by Lord Kelvin, is that radioactive action ceases at the enormous pressures inside the earth. Soddy[4] considered that Strutt's results may perhaps be evidence in favour of the view that there is proceeding in nature an as yet undiscovered process, complementary to disintegration, whereby the heavier elements are being slowly built up out of the lighter. Such a process must absorb energy in the same relatively enormous amount in which

[1] *Proc. Roy. Soc.*, 1906, **78**, *A*, 385.   [2] *Nature*, Nov. 29, 1906, 102.
[3] *Proc. Roy. Soc.*, 1906, **77**, *A*, 472.
[4] *B.A. Reports*, York, 1906 ; Evolution of the Elements, footnote.

it is evolved during disintegration. Since the heat that must be evolved in the disintegration of the known amounts of radioactive matter in the earth is far in excess of that required to maintain the loss of heat by radiation and keep the earth temperature constant, and since there is indisputable geological evidence of the constancy of the earth's temperature over a period estimated in hundreds of millions of years, there is at least now no *a priori* objection to the existence of an upbuilding process on the ground that the energy required is not available; but of course the whole subject is only at present in the speculative stage.

Eve,[1] in an examination of the radioactivity of the earth and atmosphere, showed that the ionisation of the latter is caused by the γ-radiation from the earth to the extent of only 1/16th of the total, the remainder being due to the radium emanation present in the atmosphere. He calculates the quantity of radium in the earth's crust necessary to cause the γ-radiation from the surface to be 1.8×10^{-11} gram per c.c., which is of the same order as, but about four times greater than, the average amount found by Strutt in rocks. These two widely different methods of measurement of the radium in the earth's crust are thus as concordant as can be expected considering the nature of the quantity investigated.

Advances in Experimental Methods.—An ingenious device has been suggested by Kurz[2] for reading the gold leaf of an electroscope. A circular segment is cut out of one side of the leaf near the end to be read, and a quartz fibre is waxed at the two ends and laid across the segment, and attached to the leaf by bringing a heated rod near to the wax. The quartz fibre gives a fine image for reading in the microscope. Bronson[3] has worked out a constant deflection method of using the electrometer, in which the ionisation current to be measured is proportional to the deflection of the electrometer needle instead of to the rate of movement, as in the usual arrangement. N. R. Campbell[4] has devised a null method of working in which the ionisation current to be measured is balanced against the current through a constant volume of gas ionised by a constant quantity of uranium oxide, the pressure of the ionised gas being varied. In this way the measurement is reduced to the adjustment and reading of a gas pressure.

Polonium.—The controversy as to the identity of polonium and radiotellurium, which has long ceased to present more than a nominal interest as to which of the two names should be retained, has now been ended.[5] Mme. Curie repudiated and gave convincing proof

[1] *Phil. Mag.*, 1906, [vi], **12**, 189.   [2] *Phys. Zeit.*, 1906, **7**, 375.
[3] *Phil. Mag.*, 1906, [vi], **11**, 143.   [4] *Proc. Camb. Phil. Soc.*, 1906, **8**, 132.
[5] S. Curie, *Phys. Zeit.*, 1906, **7**, 146 and 180; Marckwald, *ibid.*, 369; Meyer and von Schweidler, *ibid.*, 257.

against the idea that the polonium as first prepared and named by her gave β-rays or was in a radioactive sense heterogeneous, and protested against the period of decay as published long ago by her being accepted as giving more than the order of the time constant. A new series of exact measurements gives the period one hundred and forty days, which conforms to that of Rutherford for radium F and of numerous investigators for "radiotellurium." [1]   The greater resemblance of polonium to tellurium than to bismuth chemically is denied, and it is pointed out that in the insolubility of its sulphide in ammonium hydrogen sulphide, and of its oxide in caustic soda, polonium resembles bismuth and differs from tellurium.   Mme. Curie considers it self-evident that polonium, the first strongly active substance separated by M. Curie and herself by a method first used by them, must keep the name it received from its discoverers.   Marckwald in his communication agrees in future to use the name polonium instead of radiotellurium for his preparations, and it is to be hoped, this being the case, that the name radiotellurium will not be further used.   Meyer and von Schweidler [2] examined polonium from four different sources : (1) the residual induced activity of radium (radium F), (2) from radiolead (radium D, radium E, and radium F), (3) "radiotellurium," (4) from radioactive bismuth ("polonium"), and found that all preparations possessed substantially the same rate of decay.   The mean of the values for the period was one hundred and thirty-seven days.

Thorium.—A summary of the physical and chemical properties of the disintegration products of thorium is given by von Lerch,[3] who himself has been one of the earliest and most fruitful investigators in this field.   Our knowledge of the radiothorium, and the position of what has even come to be known as "the thorium question," has been advanced one stage further by the successful partial chemical separation of this constituent from commercial thorium compounds by Elster and Geitel [4] and G. A. Blanc.[5]   The former separated from the sediment of the hot spring at Baden Baden a preparation with all the characteristics of the thorium radioactivity, but many more times more active, the activity being permanent over short periods.   Seventy-five kilograms of these sediments from Bad Nauheim were worked up by Giesel, and gave a gram of a radium-barium preparation of strong activity but practically no thorium activity.   Twenty kilograms of the sediments from Bad Kreuznach gave, besides strong radium preparations, small quantities

[1] *Ann. Report*, 1905, 310.

[2] *Jahrb. Radioakt. Elek.*, 2, 463.

[3] *Ibid.*, 620.

[2] *Wien. Sitzungsber.*, 1906, 115 II A, 1.

[4] *Phys. Zeit.* 1906, 7, 415.

of preparations with thorium activity fifty times that of thorium. With the experience obtained in the working up of these sediments, the separation of radiothorium from commercial thorium salts was attempted. The principle of the method was to precipitate a small quantity of iron with the thorium solution, and to separate the iron from the precipitate with oxalic acid. In this way preparations were obtained decaying rapidly at first (due to the presence of thorium A and thorium B), but reaching a minimum (radiothorium only), and finally attaining a maximum twice as great (due to the reproduction of thorium X, &c.). These preparations consisted of thorium hydroxide with an activity twelve times as great as the original material. The authors point out that radiothorium, like radium, is widely distributed, being found not only in springs and in the earth, but also in some varieties of crude petroleum.

G. A. Blanc[1] first discovered that the deposits from certain hot springs at Echaillon and Salins-Moutiers possess thorium activity without any noticeable quantity of thorium being present. Very active preparations could be separated from the deposits possessing the characteristic thorium radioactivity in a very intense degree. He succeeded in separating radiothorium from ordinary thorium preparations[2] by precipitating barium as sulphate in a solution of thorium nitrate, fusing the precipitate with carbonate of soda, and precipitating the solution of the carbonates in hydrochloric acid with ammonia. A few centigrams of thorium hydroxide with a trace of iron obtained in this way had an initial activity ten times and a final activity thirty times that of ordinary thorium hydroxide. From six kilograms of thorium nitrate was obtained a few milligrams of a preparation initially strongly radioactive but free from emanating power, and ultimately developing emanating power and radioactivity 5000 times that of thorium hydroxide in equilibrium. Thus the separation from ordinary thorium compounds of radiothorium, comparable in radioactivity with the preparations obtained by Hahn from thorianite, has been accomplished; but the complete removal of the active constituent is still very far from being accomplished, and the preparation of " inactive thorium " from active thorium salts has not been effected.

The radioactivity of thorium minerals and salts has formed the subject of investigations by Dadourian[3] and Boltwood,[4] and thorium salts have also been examined from a similar point of view by McCoy and Ross.[5] The problem was to find the relation between the radioactivity of a thorium mineral or salt (due to radiothorium) and the thorium

[1] *Phil. Mag.*, 1905, [vi], 9, 118.   [2] *Phys. Zeit.*, 1906, 7, 620.

[3] *Ibid.*, 1906, 7, 453; *Amer. J. Sci.*, 1906, 21, 427.

[4] *Phys. Zeit.*, 1906, 7, 482; *Amer. J. Sci.*, 1906, 21, 415.

[5] *Ibid.*, 1906, 21, 433.

content, the thorium being in all probability itself without radio-activity. Both Dadourian and Boltwood by different methods found that the radioactivity was proportional to the content of thorium, and therefore that radiothorium must be a true disintegration product of thorium. Dadourian measured the amount of excited activity pro-duced from the solution of a given amount of a thorium mineral, and used this as a measure of the thorium radioactivity. He found this activity, and therefore the amount of radiothorium present, to be pro-portional to the thorium content of the mineral as determined by analysis. In commercial salts, however, the activity in terms of the thorium content is only about one-half of that in minerals, which points clearly to the separation of a part of the radiothorium during the processes, secret for the most part, by which thorium is com-mercially extracted from its ores. Boltwood determined the total α-ray activity of several thorium minerals, subtracted the part due to the uranium present as determined by analysis, and found for four minerals the thorium activity per gram of thorium to be a constant. Whereas the specific activity of commercial thorium salts was only one-half of that of minerals, the specific activity of the salts prepared by himself from the minerals was equal to that of the minerals. In view of what has been said (p. 361) on the labour and difficulty in separating radiothorium from thorium, and the fact that in Hahn's work only about 2 per cent. of the radiothorium probably was separated from thorianite, it will be seen that the secret commercial processes are far more effective in removing radiothorium than the known laboratory methods. An investigation of the residues in the manufacture of thorium salts commercially for the radiothorium separated had only negative results. From these researches it is placed beyond doubt that radiothorium is a disintegration product of thorium with a relatively slow period (at least several years), that the change of thorium into radiothorium is probably rayless, and therefore that inactive thorium preparations should be capable of separation. Unless the initial change of thorium were rayless, the close agreement between the results of Dadourian and Boltwood obtained by different methods would not have been shown.

Eve[1] measured the γ-rays given out by known quantities of (1) radium bromide, (2) thorianite, (3) thorium nitrate, the last two con-containing a known percentage of thorium. He found that the ratio of the γ-activity of the mineral to the salt for quantities containing similar amounts of thorium was 2·5 to 1, again pointing to the poverty of the salt in radiothorium. Hence it is to be expected that the γ-activity of a thorium salt should steadily increase with age as the radiothorium is reproduced, and an earlier suggestion that a kilogram

[1] *Amer. J. Sci.*, 1906, [iv], **22**, 477.

of a thorium salt should serve as the standard of γ-radiation is therefore to be abandoned. The γ-activity of pure radium bromide is given as 4·5 million times that of thorium oxide containing the full equilibrium amount of radiothorium.

The diffusion of thorium X in gelatin solutions has been investigated by G. Hoffmann.[1] The diffusion from an under layer to the free surface was followed by measuring the emanation from the free surface, passing a steady air stream over it. He concluded that thorium X diffuses as a single substance, and that radioactive bodies in infinitesimal quantity diffuse according to Fick's law exactly as with substances present in measurable concentration.

Actinium.—There are many problems of interest awaiting solution in connexion with this body, and the almost perfect resemblance from a radioactive point of view between thorium and actinium has been emphasised by several discoveries during the year. Hahn[2] separated a product he called radioactinium, intermediate between actinium and actinium X, and in every way analogous to radiothorium. If an ignited actinium preparation is dissolved in hydrochloric acid the residue contains relatively a greater proportion of the radioactinium than the solution. A complete separation of the product is obtained when actinium, freed from actinium X by repeated precipitation with ammonia, is treated with sodium thiosulphate in acid solution. Amorphous sulphur is precipitated, and carries down the radioactinium only. Another method is also given depending on the partial precipitation of actinium with ammonia when the active radioactinium is concentrated in the precipitate. The ranges of the various α-rays have already been given (p. 343), and also the conclusion that actinium B is the only β-ray product (p. 340). The period of radioactinium is given as twenty days, and actinium freed from this and the later products possesses no activity, so that the initial change is rayless as in the case of thorium. Godlewski in his separation of actinium X[3] separated unawares some of the radioactinium as well as the actinium X, which accounts for the low activity of the actinium recorded by him. Hahn obtained no evidence of the existence of any residual activity in the case of actinium excited activity pointing to the existence of a possible actinium D, &c., analogous to radium D, radium E, and radium F. On the other hand, Meyer and von Schweidler[4] detected a small residual activity, $\frac{1}{10000}$th of the initial, after the ordinary induced activity, produced from the actinium emanation after forty-eight days' working, had been allowed to decay. But instead of being

[1] *Ann. Physik.*, 1906, [iv], **21**, 239.
[2] *Ber.*, 1906, **39**, 1605; *Nature*, April 12, 1906, 559; *Phys. Zeit.*, 1906, **7**, 855.
[3] *Ann. Report*, 1905, 307.
[4] *Wien Anzeiger*, 1906, 12; *Sitzung.*, April 26.

of a slow period, as in the case of radium, which is to be expected of a product so relatively feeble in activity, it decayed regularly with a period of $11\cdot7$ days. The ordinary view leads us to expect that the product of the activity into the period should be approximately the same for all the successive members of a true disintegration series, but the case in question, and also the other new cases of the α-radiation of uranium X and thorium A, and the β-radiation of radium B, constitute exceptions to this rule. We are faced with several examples of ray changes in which the total radiation emitted is very much less than in other cases for changes in the same disintegration series. The most important example of this is probably actinium itself.

Boltwood [1] examined the relative proportion of the α-ray activity of radioactive minerals due to the separate radioactive constituents, and found it could be expressed as the sum of two factors, one depending on the amount of uranium, and the other on the amount of thorium present. McCoy [2] found that the total radioactivity of five uranium minerals not containing thorium was proportional to the content of uranium being always $4\cdot15$ times the activity of the uranium present. This means that actinium must be a product of uranium, and that all the radioactive constituents must be successive members of two series, that of uranium and that of thorium.

The quantity of actinium, determined by separating it from the mineral, is proportional to the uranium. The conclusion was drawn that actinium must be a disintegration product of uranium. But Rutherford and Boltwood, in an examination of the activity of uraninite, found that it was almost accounted for by the radium and uranium present, so that the actinium contributes but a small fraction of the total activity. Yet since actinium gives four α-ray products in its disintegration to five furnished by radium, it is to be expected that the activity contributed by actinium should be comparable to that furnished by radium. In these circumstances Rutherford [3] was inclined to view actinium as a simultaneous side-product out of the main line of descent, a suggestion similar to that proposed in the case of radium A and radium B, and since shown to be unnecessary. Here also the most recent development seems against the view. Boltwood [4] separated as completely as possible the actinium from a kilogram of carnotite, and measured the amount of radium present in the actinium solution at first, and again 193 days later. In this interval the quantity of radium was found to have increased from $5\cdot7$ to $14\cdot2$ ($\times 10^{-9}$ gram), and the conclusion was drawn provisionally that actinium is the

    [1] *Phys. Review*, 1906, **22**, 320.   [2] *Phil. Mag.*, 1906, [vi]. **11**. 177.

    [3] *Radioactive Transformations*, p. 177.

    [4] *Nature*, Nov. 15, 1906, p. 54; *Amer. J. Sci.*, 1906, **22**, 537; *Phys. Zeit.*, 1906, **7**, 915.

parent of radium, and that the rate of production is approximately what is to be expected on the view that all the radium in a mineral results from the change of the actinium present. This, if confirmed, shows that actinium is in the main line of descent, and the relations of theory and fact have assumed a kind of stalemate.

Radiolead.—This substance, it is now quite clear, owes its activity to the presence of radium E (β-rays) and radium F (α-rays) formed from and in radioactive equilibrium with radium D (rayless). Although the initial change of radium D is slow, the succeeding changes are more rapid, so that the preparation rapidly grows in α- and β-activity, and reaches an equilibrium after a year or two. Meyer and von Schweidler by electrolysing the acetate solution with a current-density of four microamperes per sq. cm. separated polonium (radium F). With ten microamperes both polonium and radium E are deposited, and with 100 microamperes radium D also as well as lead separates. The period of radium E is given as 5·02 days. Giesel in his paper on β-polonium gives a somewhat higher period, 6·14 days, whilst Rutherford in his original paper gave 4·5 days.

Elster and Geitel,[1] starting from the observation of N. R. Campbell, that the natural ionisation inside lead vessels is abnormally large, and of A. Wood,[2] that no emanation is given out by lead solutions, and that the radiations from lead possess a greater penetrating power than the α-rays of radium, made a thorough examination of the activity of ordinary lead. They found that surrounding a zinc vessel with a lead mantle reduced the natural ionisation 11 per cent., showing that the lead gives no appreciable penetrating radiation, but absorbs the penetrating radiation from the earth discovered by Cooke. A kilogram of radiolead obtained from Giesel gave no radium emanation, although the minutest amount could be detected. Using methods which would effect the separation of the radioactive constituents from radiolead, they succeeded in separating from ordinary commercial lead salts preparations with feeble activity. The lead was precipitated successively with hydrochloric acid, sulphuric acid, and hydrogen sulphide, and the last minute precipitate of lead sulphide was feebly active and resembled radiolead. Since radium is very frequently contained in lead ores, it is possible that the radium D, which resembles lead chemically, is separated with the lead and is the cause of its feeble activity. This suggests to the authors an elegant piece of work, for old lead—for example, that obtained from the roofs of old buildings—should not be active, as the radium D would all disappear in two or three centuries, and unless the lead actually contained radium itself, its activity after this period should have completely decayed.

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